LABORATORY EXERCISES IN APPLIED CHEMISTRY

FOR STUDENTS IN TECHNICAL
SCHOOLS AND UNIVERSITIES

MOLDENHAUER

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BY

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AUTHOR'S PREFACE

Although technical analysis has long been included in the curricula of technical colleges, a textbook devoted solely to this subject is still lacking. Laboratory manuals and the like generally contain little more than mere descriptions of technical methods of analysis, and explanations of the underlying chemical principles or of their applications are seldom attempted. It is evident that such books can be of very little help to students. The mechanism of the reactions involved in analytical methods is by no means so clear that explanation is unnecessary, since a student usually begins technical analysis at a comparatively early stage in his course. Neither can it be assumed that the student has sufficient knowledge of the practical side of the subject to enable him to grasp the full significance of the analysis in which he is engaged. Only when the analyst understands what part the raw material under examination is destined to play in subsequent industrial operations, how a manufactured product has reached its final condition and for what purpose it is to be used, is he in a position to appreciate the importance of the various determinations, or the consequences that might ensue from a faulty analysis. The author, as lecturer in the Darmstadt Technical School, knows from his long experience that it is just the emphasis laid upon the technical application of an analysis which deepens the student's knowledge and understanding of chemical processes. Interest is stimulated in the analysis itself, which is thus saved from being regarded merely as an unnecessary extension of ordinary quantitative analysis. The book of exercises now presented originated in a desire to produce a really useful laboratory book which should meet the requirements of students, and for this reason it is not only provided with such chemical explanations as seem essential to the clear understanding of the methods themselves, but is also well supplied with notes on the technology of the subject. It comprises practically all the exercises included in the course of study at the local Technical School. These have been selected in such a way that the student is made familiar with the best and most characteristic examples of technical methods of analysis, and at the same time he obtains a general view of the most important branches of the chemical industry. The contents of this book can be mastered by a diligent and capable student in six months. If, during the progress of the experiments in the laboratory, he makes use of his leisure moments to read through the explanations and remarks attached to the exercises, the purpose for which the book was written will have been completely achieved.

W. MOLDENHAUER

DARMSTADT.

TRANSLATOR'S NOTE

In preparing this translation from the first German edition a few notes of purely local interest have been omitted, while others have been added where necessary. The latter are indicated in the text.

The translator desires to express his thanks to Messrs. A. T. Green and H. V. Thompson, M.A., for valuable assistance in reading through the manuscript and proof-sheets.

L. B.

Stoke-on-Trent,
1921.

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LABORATORY EXERCISES IN APPLIED CHEMISTRY

GENERAL PART

Scientific and Technical Analysis.—There is no fundamental difference between scientific and technical analysis. The analyst in a technical laboratory frequently has to apply the methods of the scientific laboratory to the investigation of commercial materials. This is generally done when there is no particular reason for hastening the analysis, and when extreme accuracy is the most important factor, as in the testing of valuable ores or expensive raw and manufactured products, where large quantities of material have to be valued correctly on the analysis of a single average sample.

The case is entirely different, however, when the analysis serves for the control and regulation of works operations. Here the results are required quickly, and methods of analysis must be chosen accordingly, even at the risk of inaccuracy. In such cases scientific accuracy is generally of little importance, a rough estimation sufficing for practical purposes.

Other demands are made on technical methods in commercial laboratories and agricultural experimental stations. Here the analysis is not valued for its precision, and the work of these establishments would be unremunerative if the analyst had to devote the same amount of time to his investigations as the chemist in a scientific laboratory. Methods suitable for such institutions must be simple and expeditious, while capable of giving reliable results. The rapidity with which results are often obtained in commercial laboratories is, however, not entirely due to the methods employed, but partly to routine and to the use of specially designed apparatus.

Sampling.—The sampling which precedes every technical analysis must be done with the greatest circumspection and care. An analysis, accurate in itself, is quite worthless if the sample analyzed does not represent the average composition of the whole of the material under examination. The sampling of liquids is comparatively easy. It is obvious that hygroscopic or easily oxidizable liquids should not be unduly exposed to the air, also that the sample should not be taken merely from the surface. Similarly, drinking-water or feed-water, in which the amount of oxygen or free carbonic acid is to be determined, should not be left in contact with air for any considerable time. The concentration of thick, viscous fluids may vary in different horizontal layers. If a complete mixing of the whole liquid is impracticable, a number of samples should be taken as uniformly as possible from the various layers, mixed, and shaken well together before use.

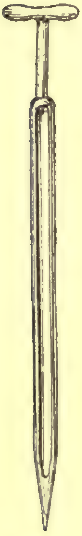


FIG. 1.

For sampling large quantities of finely divided solids a special instrument, known as the "slotted pipe sampler," or "sampling stick," has been devised (Fig. 1).

This consists of a long hollow shaft of thin sheet iron slotted down one side, with a handle at the top, and terminating downwards in a sharp point. In taking the sample, the borer is pushed deeply into the barrels, sacks or heaps of the material, and turned once round on its axis. On drawing it out, a sample is obtained which comes uniformly from every layer. This manipulation is performed at several places in the heap according to the quantity of material available, the separate probes being mixed together and taken for analysis.

A good average sample of lumpy material is obtainable only with difficulty. In this case the sampling is usually done during the loading and discharging of the material, a portion weighing several kilograms being taken from each truck or barrel. The larger and less uniform the pieces, the greater must be the weight of the sample taken. Care should also be exercised that the sample contains equal proportions of the coarse and fine material, since the composition of the latter is often notably different from that of the lumps. The sample thus obtained is roughly broken up, either by hand or in a mechanical crusher, mixed thoroughly together and spread out in a thin layer, from which a small portion of a few kilograms is taken. This is crushed still finer, mixed, and quartered in the usual way, the operation being repeated until a conveniently small sample is obtained.

Further Preparations for Analysis.—Ores and other hard substances, if not already in such a fine condition that they can be pulverized directly in an agate mortar, are first ground in a small ball-mill, roller crushing-mill, or iron mortar. Substances which are not readily soluble and require fusion with sodium carbonate should be sifted through a silk lawn. The analyst should make a practice of sifting the whole of the material in the mortar, leaving no residue. When only a portion is sieved and the rest rejected, there is always the danger of the more friable constituents of the mixture being separated from the harder ones, thus altering the composition of the sample. Very hard substances like chrome iron ore and iron alloys, which are extremely difficult to disintegrate, can be ground in an agate mortar, but are best treated in a mortar of hardened steel having the form shown in Fig. 2. The lower part of the apparatus (*c*) is bored out in the form of a cylinder having a diameter equal to that of the stamp *a*. This opening is widened slightly at the top to allow the guiding ring (*b*) of the stamp to enter a little way. A small quantity of the material to be powdered is placed in *c* and, after adjusting the ring and stamp, the latter is given a series of sharp blows with a heavy hammer. From time to time the powdered substance is shaken out on a sheet of clean paper

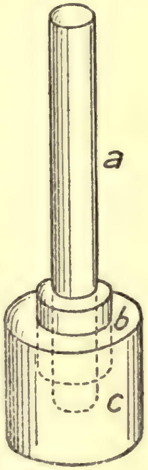


FIG. 2.

and sieved, the coarser residue being put back again in the mortar; this operation is repeated until the whole of the material passes through the sieve, leaving no residue.

The method of disintegrating iron is described in the Special Part, p. 150.

Such substances as cereals, beans and peas, which are required in a fine state of division for the estimation of nitrogen or water, and cannot easily be handled in mortars, are best treated in an ordinary coffee-mill.

Weighing.—The delicate balances, indicating to 0·1 milligram, employed in general analysis are also largely used in technical laboratories, but for many purposes less sensitive instruments serve sufficiently well. When a good average sample is required, the following method is commonly employed in the case of easily soluble substances: A comparatively large amount—10 to 100 grams—of the substance is dissolved (or, more rarely, suspended) in water, and an aliquot portion of the solution or suspension taken for the analysis. By this method a balance sensitive to 0·01 gr. can generally be used, even when the material contains only a small percentage of the constituent to be estimated. For instance, if 10 grs. of the substance be weighed out with an error of 0·01 gr., the final error on a 50 per cent. constituent will be 0·05 per cent., on a 10 per cent. constituent 0·01 per cent.; if three or five times this amount of substance be weighed out, the ultimate error will be three or five times smaller, and so on. It is clear that under these conditions the error in weighing is insignificant compared with errors arising from the various analytical manipulations, and by weighing in this way much time is saved. For rapid weighing the small hand-scales with horn-pans, commonly used by apothecaries, can be employed with advantage. A superior balance of this class is accurate to 0·01 gr.

In technical laboratories where the same analysis is performed day after day it is usual, in order to simplify the calculation of results, to weigh out such a quantity of the sample that the percentage of the constituent determined is given directly by the weight of the precipitate. Thus, in the potash industry, for the determination of potassium by the platinum chloride method, 30·56 grs. of the raw salt are weighed out when the percentage of potassium is to be expressed as chloride, or 35·71 grs. when it is stated in terms of sulphate. Of this amount only 1·00 per cent.—*i.e.*, 0·3056 gr. (or 0·3571 gr.)—is used for the analysis, so that every milligram of potassium chloroplatinate obtained corresponds to 0·1 per cent. of potassium chloride or sulphate. In such cases special weights are provided; thus, for the potassium determination weights of 30·56 grs. and 35·71 grs., which add greatly to the convenience and accuracy of weighing.

Analytical Devices.—As already stated, any protracted operation renders a method unsuitable for use in technical laboratories, and for this reason many devices are adopted to speed up the analysis. For instance, the usual practice of allowing the magnesium ammonium phosphate precipitate to stand for eight to twelve hours is avoided by stirring the solution vigorously (as described more exactly in the Special Part), whereby a quantitative precipitation is achieved in twenty minutes. For washing precipitates which are difficult to filter, such as the hydroxides of iron, aluminium, or chromium, Lunge recommends the use of almost boiling water. Where it is necessary to separate a precipitate which is not required for further examination, the washing can nearly always be avoided in practice by precipitating in a graduated flask, filling up to the mark and taking an aliquot portion of the clear solution, decanted through a dry filter-paper. In this way, not only is the time required for washing saved but subsequent evaporation is also avoided, as the filtrate is not diluted with wash-water.

The error due to the volume of the precipitate is, in most cases, negligible. If this volume be very large, a suitable correction is made by filling the flask correspondingly above the mark. In consequence of absorption, a filter always retains a certain amount of salt from the solution; for this reason the first few cubic centimetres of the filtrate, which have a slightly different concentration, should be rejected. A typical example of the treatment of precipitates in this way is presented by the determination of potash in organic and inorganic manures, as described in the Special Part, where several times in the course of an analysis the suspension is diluted to the mark and filtered without washing.

Whenever practicable, instead of drying the precipitate on the filter in an oven, the paper should be freed mechanically from the greater portion of its moisture by gently pressing it on a second *dry* filter, after which it is ignited moist in a platinum or porcelain crucible. Precipitates of silica, barium sulphate, calcium oxalate, and magnesium ammonium phosphate, treated in this way give quite as good results as if previously dried.

For some years *Neubauer* crucibles prepared after the manner of the well-known Gooch crucibles, with spongy platinum in place of the customary asbestos wad, have been extensively employed. The crucibles themselves are made of porcelain or, better, of platinum, and the precipitate can be heated to redness in them. By this method it is usual to carry out a whole series of determinations without cleaning the crucible—*i.e.*, the fresh precipitate is filtered through that of the same constituent already in the vessel, thus saving cleaning, drying and reweighing the crucible once for every analysis.

In cooling the crucible, it is customary in technical practice to place it in a desiccator only when the precipitate is of a hygroscopic character, otherwise it is laid on a cold slate or metal plate, and is then ready for weighing after quite a short time.

The heating appliances in industrial laboratories are precisely the same as those in scientific laboratories. The modern *Méker* burner, which gives a flame considerably hotter than that of the ordinary Bunsen or even the *Teclu* burner, renders the use of the blowpipe unnecessary in most cases. Fig. 3 represents a section through such a burner. By means of a metal cap *C* (shown in plan to the right) placed in the tube *B*, so large a cooling surface is obtained that, although the gas is mixed in the tube with sufficient air for complete combustion, the flame cannot strike back. The flame burns without the familiar cold blue zone of the Bunsen flame, and attains the highest possible temperature immediately above the burner. In works laboratories small gas muffles, which are capable of holding a number of crucibles and require little attention, are also largely used. Fig. 4 shows a favourite form of this type of mfflue. Laboratories which are not supplied with gas employ spirit lamps or benzene Bunsen burners, and also small muffle furnaces heated with coke. Where electric current is available, an electrically heated crucible furnace may be recommended. These furnaces permit a very exact regulation of the temperature and consume but little power.

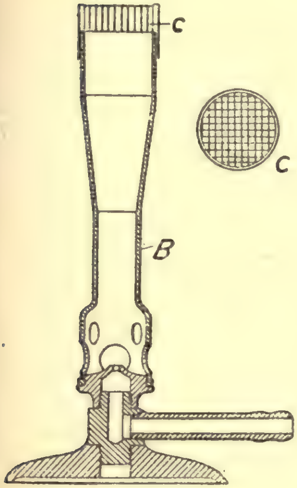


FIG. 3.

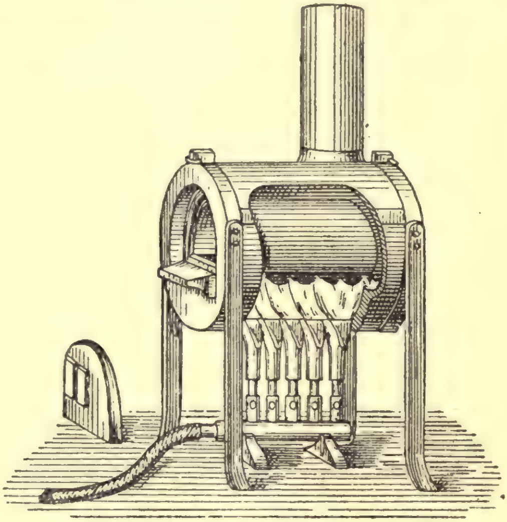


FIG. 4.

Volumetric Analysis.—Volumetric methods are preferable to gravimetric when they yield sufficiently accurate results. There are a large number of titration methods in use in technical practice which find no place in scientific laboratories (*e.g.*, the titration of zinc by the methods of Schaffner or Galetti, of lead by Alexander's method, or the titration of phosphorus in iron). In laboratories where many titrations are performed, burettes which can be filled automatically to the zero-point are provided. Such an arrangement is shown in Fig. 5. By means of a rubber bulb the standard solution is forced into the burette, which is placed directly above a large storage-bottle having a capacity of several litres. On the air pressure being released, the solution flows back exactly to the zero mark. A small tube filled with cotton-wool may be interposed between the bulb and the bottle to catch any dust, or, when working with alkalis, a similar tube of soda lime may be used to absorb the carbon dioxide from the air. If the stock solutions are affected by oxygen, the burette can be filled by forcing in carbon dioxide, and so on. The analyst in a technical laboratory must satisfy himself as to the accuracy of the measuring vessels, as he would in a scientific laboratory, and he should note how the pipettes are graduated, whether for ordinary delivery or blowing out. Whenever possible, the amount measured out should be such that the percentage composition can be ascertained directly from the number of cubic centimetres used without further calculation. For instance, if bleaching powder is to be titrated with arsenious acid, 7·1 grs. of the former are dissolved in 1,000 c.c. of water, and 50 c.c. of this solution, containing 0·355 gr. of substance, are taken for each titration. Since 1 c.c. of decinormal arsenious acid is equivalent to 0·00355 gr. of available chlorine, 0·1 c.c. of the standard solution thus corresponds to 0·1 per cent. of available chlorine.

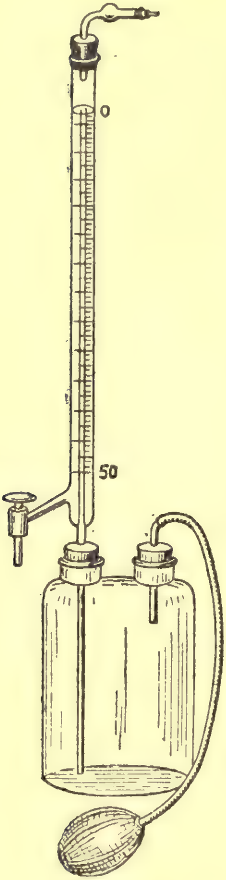


FIG. 5.

Specific Gravity Determinations.—Specific gravity determinations are often used as a means of estimating the composition of liquids, and are especially useful as controls in the manufacture of sulphuric, nitric and hydrochloric acids. Many liquids are valued commercially according to their specific gravity; indeed, in certain cases—*e.g.*, the determination of alcohol in wines and spirits—this is the only available method.

The specific gravity is occasionally determined by means of the pyknometer or the Westphal balance, but hydrometers (floats) are generally employed. The stems of these instruments are graduated to show the specific gravity either with reference to water=1, or more frequently according to some arbitrary scale, giving a direct reading of the percentage composition of the liquid under examination.

In the German chemical industry the *Baumé* scale (written ° Bé) is employed for liquids which have a specific gravity greater than unity. The zero-point on the Baumé scale is the specific gravity of distilled water at 12·5° C, and 10 degrees corresponds to a 10 per cent. solution of common salt. The stem between these marks is divided into ten equal intervals, the graduations being continued above the 10° mark. In England the *Twaddell* degree is often used, which is obtained from the specific gravity by the formula Tw°=(sp. gr. − 1)×200. The following table shows the corresponding values on the two scales:

Spec. Grav. at 15°/4°.	*Degrees Baumé.*	*Degrees Twaddell.*
1·000	0·0	0
1·050	6·7	10
1·100	13·0	20
1·150	18·8	30
1·200	24·0	40
1·250	28·8	50
1·300	33·3	60
1·350	37·4	70
1·400	41·2	80
1·450	44·8	90
1·500	48·1	100
1·550	51·2	110
1·600	54·1	120
1·650	56·9	130
1·700	59·5	140
1·750	61·8	150
1·800	64·2	160

Certain hydrometers are graduated in a special way for particular determinations; thus the *alcoholometer* indicates the number of grams of absolute alcohol in 100 grs. of the liquid at 15° C., and the *saccharometer*, marked in Balling-Brix degrees, gives a direct reading of the percentage of pure cane sugar in an aqueous solution.

Very accurate determinations can be made with hydrometers of superior construction, but attention should be directed to the following points: The hydrometer must be dipped in the liquid slowly, so that the portion of the stem which projects above the surface is kept dry; otherwise considerable error may arise, particularly in the case of viscous liquids. The instrument must float quite freely out of contact with the wall of the cylinder (which should not be too narrow). The reading should be taken at the point where the hydrometer intersects the surface of the liquid; thus along the line A_1, A_2 (Fig. 6), regardless of the meniscus formed (line B_1, B_2). The temperature of the liquid to be tested should be carefully adjusted to that given in the specific gravity table, and a hydrometer graduated for use at this particular temperature is required. As a rule the tables are constructed for 15° C., and are based on the specific gravity of water at $+4^\circ$ C. $= 1$. Frequently, however, water at a temperature of 0° or 15° C. is taken as a standard. The unit of comparison and the temperature at which the instrument is to be used are generally marked on the stem. These data are indicated by $\frac{15^\circ}{0^\circ}$, or $\frac{15^\circ}{4^\circ}$, or $\frac{15^\circ}{15^\circ}$, the number above the line representing the temperature for which the instrument is graduated, that below the line the temperature of the water at which the specific gravity is taken as unity. If the values given in the table do not coincide with those on the hydrometer, a correction is necessary. Suppose that the table is constructed for $\frac{15^\circ}{15^\circ}$, and the

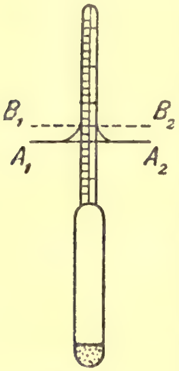


Fig. 6.

hydrometer is graduated for $\frac{15^\circ}{4^\circ}$, since the specific gravity of water at a temperature of 15° is only 0·9991, the hydrometer readings will be too low, and must be divided by 0·9991 to bring them into agreement with the table. Conversely, if the table is based on $\frac{15^\circ}{4^\circ}$ and the hydrometer on $\frac{15^\circ}{15^\circ}$, the reading of the instrument will be too high, and must be multiplied by 0·9991 in order to compare with the table.

Mistakes often arise through not taking care to observe whether the values given in the table refer to percentage by weight or by volume. "*Percentage by weight*" indicates the number of grams of a substance contained in 100 grs. of the liquid; "*percentage by volume*," as a rule, the number of cubic centimetres of pure liquid substance contained in 100 c.c. of the solution. To convert percentage by weight into percentage by volume, the former is divided by the specific gravity of the pure liquid and multiplied by the specific gravity of the solution. An example will make this clear: An aqueous solution of alcohol containing 50 per cent by weight has a specific gravity=0·91865 at 15° C., that of pure alcohol at the same temperature being 0·79425; 100 grs. or $\frac{100}{0 \cdot 91865}$ c.c. of the solution contain, therefore, 50 gr. or $\frac{50}{0 \cdot 79425}$ c.c. of pure alcohol, and 100 c.c. of the solution $\frac{50 \times 0 \cdot 91865}{0 \cdot 79425}$ c.c.=57·9 per cent. by volume.

Frequently, however, the amount of dissolved gases or dissolved solids is also expressed in percentage by volume, by which, in this case, we understand the number of grams of the dissolved substance in 100 c.c. of the solution. Here the conversion of "percentage by weight" into "percentage by volume" is effected simply by multiplying the former by the specific gravity of the solution. Thus, an aqueous solution of hydrochloric acid having a specific gravity=1·10 at 15° C. contains 20·01 per cent. by weight of hydrochloric acid (see table in Appendix), or 20·01×1·10=22·01 per cent. by volume. In such cases, however, it is best to avoid the expression "percentage by volume," and to state the result in grams of substance per litre; thus, in the present example as "220·1 grs. hydrochloric acid per litre."

Technical analysis involves the use of acids of widely different concentrations, and the student should endeavour to make himself familiar with those commonly provided in laboratories. The relation of the concentration to the specific gravity should also be noted, especially in the case of hydrochloric, nitric and sulphuric acids.

The ordinary concentrated hydrochloric acid of the laboratory has generally a specific gravity of 1·124, corresponding to about 24·8 per cent. by weight of HCl. Stronger acid fumes in the air. The laboratory fuming hydrochloric acid is a product almost saturated with hydrochloric acid gas at ordinary temperatures; it has usually a specific gravity of 1·19, and contains about 38 per cent. by weight of hydrochloric acid.

As a working rule we may note that the percentage by weight of hydrochloric acid can be found approximately from the specific gravity by the formula (sp. gr. $-$ 1) $\times$ 200, since in this particular case the percentage by weight corresponds almost exactly to the number of Twaddell degrees.

The ordinary concentrated nitric acid of the laboratory contains about 70 per cent. of HNO_3, and has a specific gravity of 1·42. Highly concentrated nitric acid is generally strongly coloured with oxides of nitrogen; as a rule it contains 90 to 97 per cent. HNO_3, and its specific gravity is about 1·5. An acid having a specific gravity of 1·2, containing 32 per cent. by weight of HNO_3, is also frequently used in technical analysis.

Finally, the concentrated sulphuric acid of the laboratory has a specific gravity of 1·83 to 1·84, and contains 95 to 98 per cent. by weight of H_2SO_4.

A rough approximation of the percentage of H_2SO_4 in acids of specific gravity 1·3 to 1·6 is obtained by disregarding the whole number and adding ten to the first two decimals. Thus, an acid of specific gravity = 1·35 contains about 45 per cent., one of specific gravity = 1·50 about 60 per cent. H_2SO_4, and so on.

The percentage compositions of the three acids just mentioned, loosely termed "concentrated" in the laboratory, are thus entirely different. The individual concentrations, however, are not the result of chance, but are closely connected with the properties and methods of preparation of these acids.

Aqueous solutions of volatile acids exhibit a certain common behaviour. When a weak solution is heated, the concentration gradually increases and the boiling-point of the solution rises. Presently the boiling-point becomes steady, and when this stage is reached no further alteration in the concentration takes place, the mixture distilling unchanged, just as if it were a homogeneous compound. Conversely, if a very strong solution be heated, a greater proportion of acid than of water distils over at first, the residue thus becoming more dilute, while the boiling-point rises as before. But when the concentration of the constant-boiling mixture is reached, the composition of the distillate becomes uniform. Thus, the concentration of the final product is always the same, however different that of the original solution may have been.

The constant-boiling mixtures were at one time supposed to be definite hydrates, but this view has been refuted by the discovery that an alteration of the pressure produces a change in the composition of the distillate.

The similar behaviour of hydrochloric, nitric, and sulphuric acids is shown in the diagram (Fig. 7). It is known that the ordinary pure concentrated nitric and sulphuric acids of the laboratory are practically identical with the constant-boiling mixtures. In the case of hydrochloric acid the conditions are somewhat different. The constant-boiling acid contains only 20 per cent. of HCl. If, however, a current of air or other neutral gas be passed through aqueous hydrochloric acid of any given concentration at about 15° C., the dilute acid gives up an excess of water vapour, and its concentration increases to about 25 per cent.; conversely, a more concentrated acid gives up a greater amount of hydrochloric acid gas than of water, and its concentration falls to the same value. Thus, a concentration of about 25 per cent. is always reached, so that the concentrated hydrochloric acid of the laboratory, which has this composition, may be regarded practically as a constant-boiling mixture at 15° C.

Calculation of Results.—In general, results should be stated to two places of decimals, the third figure, which is taken into account only in exceptional cases, being rounded off. The use of superior slide-rules, which allow the result to be read with sufficient accuracy, is recommended; these save the student from the unscientific practice of calculating his analysis to five or seven places.

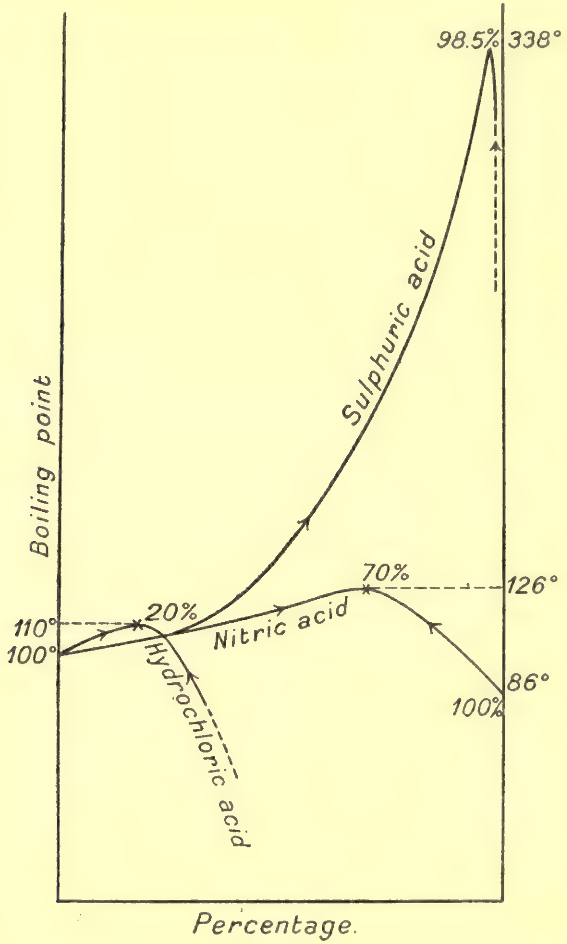


FIG. 7.

SPECIAL PART

1. COAL.

THE coal used in the following determinations should be finely ground. For sampling see p. 2.

1. Determination of Moisture.—About 10 grs. of the sample are weighed in a shallow weighing-bottle, or covered watch-glass, and heated at 105° C. for two hours. After allowing to cool in a desiccator, the loss is determined.

The drying should be done as far as possible in absence of air (for very accurate determinations, in an atmosphere of hydrogen or carbon dioxide), since many kinds of coal undergo slight oxidation at the drying temperature. Dry coal is hygroscopic; hence the necessity for weighing in a closed weighing-vessel.

The amount of moisture in coals decreases with their geological age—*i.e.*, the more completely the vegetable matter is decomposed, the less water the coal contains. Gas coals may contain up to 7 per cent., anthracite coals seldom more than 1 to 2 per cent. of moisture.

2. Determination of Ash.—2 to 3 grs. of the sample are incinerated in a shallow dish (preferably a silica tray), heated in a gas muffle or in a crucible placed slantwise over a Bunsen burner. At first the heating should be very gradual to prevent spurting (where much moisture or volatile matter is present) or sintering in the case of caking coals. Finally, the crucible is raised to a dull red heat. The burning of the carbon is assisted by stirring with a platinum wire. To test whether incineration is complete, the sample is cooled and moistened with absolute alcohol; any unburnt particles of carbon float on the surface and are easily detected. After driving off the alcohol, the crucible is cooled in a desiccator and weighed.

The mineral matter, or ash, is not derived to any considerable extent from the original plant substance, but consists mainly of sand and clay deposited amongst the living or decaying vegetation. For this reason it varies greatly in amount and chemical composition. Coal ash is distinguished from wood ash by a relatively high percentage of alumina and the absence of potassium salts, which are leached out during the process of decay. The chief constituents of coal ash are silica, alumina, oxide of iron, and lime. The proportion in which these are present influences the clinkering property of the coal. Strong slagging may be expected when the proportion of silica to iron oxide and lime favours the formation of easily fusible double silicates, while a large excess of either the acid (SiO_2) or the basic oxides will reduce the tendency to clinker.

3. Determination of Coke.—1 gr. of *undried* coal is heated in a platinum crucible, supported on a platinum triangle over a Bunsen burner, until combustible gases no longer escape between the rim of the crucible and the lid. The sample should be heated for exactly ten minutes. Without removing the lid, the crucible is allowed to cool in a desiccator and the loss determined. This loss, minus the moisture content, represents the volatile combustible matter. The yield of coke is calculated on ash-free coal.

The flame of the Bunsen should be at least 18 cm. high, and the bottom of the crucible 3 cm. above the mouth of the burner.

It is important that the conditions should be precisely the same in every experiment.

In place of platinum, a thin-walled nickel crucible, though not so serviceable, may be employed.

Coke is the residue from the dry distillation of coal—*i.e.*, from coal heated out of contact with air. The amount of coke obtained from any particular sample varies with the conditions of heating. Thus, if the temperature be raised slowly, the moisture in the coal is expelled without decomposition, while rapid heating favours the interaction of steam and carbon, whereby a part of the latter is oxidized and carried off:

$$C + 2H_2O = CO_2 + 2H_2,$$

or

$$C + H_2O = CO + H_2.$$

Again, the composition of the hydrocarbons formed depends upon the temperature at which the distillation takes place, so that a given quantity of hydrogen in combination may remove different amounts of carbon. Hence, a uniform method of heating is adopted, by which concordant results may be obtained. Successive experiments with the same sample of coal should agree to within a few tenths per cent.

The amount and physical character of the coke residue afford some indication of the suitability of a coal for any particular purpose. The richer a coal is in gas-forming constituents, the smaller the yield of coke; thus the richest gas coals may leave as little as 50 per cent., the anthracite coals upwards of 90 per cent. of residue.

Many kinds of coal fuse on heating, forming a compact lustrous cake. These are especially suitable for the preparation of dense metallurgical coke, and are termed "caking coals" or "fat coals." Others, the so-called "free-burning" or "lean coals," leave powdery residues. Between these extremes are the open-burning, long-flame coals, with their corresponding intermediate grades of coke.

The coking properties of a coal are not governed by its richness in volatile matter. Some caking coals have approximately the same composition as lean coals. Caking depends upon the presence of certain organic substances which decompose on heating, forming a kind of pitch, whereby the carbon residue is cemented.

4. Determination of Sulphur (Eschka's Method).—1 gr. of the sample is mixed thoroughly in a platinum crucible with 1 gr. of calcined magnesia and 0·5 gr. of anhydrous sodium carbonate, and gradually heated to redness over a Bunsen burner. To ensure an efficient circulation of air, as also to prevent access of sulphur compounds from the gas flame, the crucible, instead of being supported in the usual way, is fixed in a hole of suitable size through a sheet of asbestos tilted at a slight angle. The mass should be stirred occasionally with a platinum wire. When the carbon has been completely burnt off, the residue, after cooling, is emptied into a beaker containing about 50 c.c. of water, and the crucible is carefully rinsed out. Sufficient bromine water to produce a permanent yellow coloration is added, and the solution boiled for a few minutes. The insoluble matter is then filtered off and washed. The filtrate and washings are just acidified with hydrochloric acid and boiled to expel the bromine, after which the sulphate is precipitated in the usual way by the addition of barium chloride.

Fresenius' well-known method of oxidizing sulphur by fusion with a mixture of sodium carbonate and potassium nitrate cannot be employed here, since the nitre would react too energetically with the carbonaceous matter.

In this case the oxidizing agent is atmospheric oxygen; the addition of magnesia produces an infusible porous mass through which the air passes freely.

The sodium carbonate employed should be thoroughly dehydrated to prevent the formation of lumps. Magnesia frequently contains sulphates. Both these reagents should be tested for sulphur before use and, if necessary, an allowance made from a blank determination. The sulphur in coal occurs in three forms—(1) as pyrites; (2) as sulphates, mainly gypsum; (3) as organic compounds. A special determination of these different forms, described in some books, is of little practical value.

In whatever form it exists, sulphur must be regarded as an objectional element in coal. The corrosive action of sulphurous gases on boiler plates and fittings is well known.

In the dry distillation of coal some of the sulphur is expelled in the form of hydrogen sulphide and organic sulphur compounds, but the major portion remains in the coke. Coke containing much sulphur is unsuitable for most metallurgical operations, while the presence of this element in illuminating gas adds greatly to the trouble and expense of purification.

5. Determination of Hydrogen and Carbon.—These elements are determined by ultimate analysis. The coal is burnt in a current of oxygen to water and carbon dioxide, which are absorbed in weighed tubes of calcium chloride and soda lime. The apparatus is shown in Fig. 8. It consists of a hard-glass tube packed for a distance of about 10 cm. with granulated lead chromate, succeeded by a layer of about 30 cm. of oxidized copper wire. The tube is placed in a Liebig or Dennstedt combustion furnace. Any traces of moisture are first removed by heating the tube uniformly along its whole length and passing through it a current of dry air (free from carbon dioxide), after which the rear half of the tube is allowed to cool with a guard-tube of calcium chloride inserted in the open end.

Meanwhile about 0·2 to 0·3 gr. of the finely powdered sample is weighed into a small boat. For this purpose it is best to use undried coal, calculating the amount of dry substance from determination (1). The absorption-tubes are also weighed and connected up.

When everything is in readiness, the copper oxide and lead chromate are heated to redness with the cover-plates down; the boat is introduced as quickly as possible, and a slow current of air passed through the tube. The flame is then lighted beneath the boat, which is gradually heated until the coal begins to glow. When the main reaction has subsided, the current of air is replaced by oxygen and the boat is strongly heated (eventually with the cover-plate down) until incineration is complete.

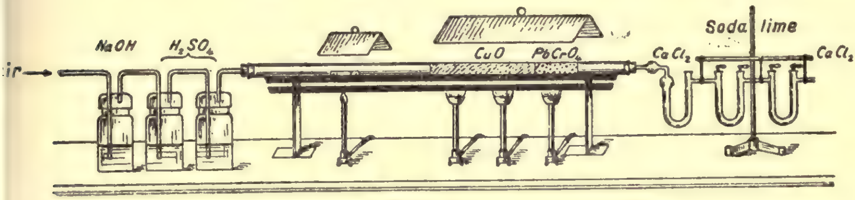


FIG. 8.

6. Determination of Nitrogen.—About 1 gr. of finely powdered coal is decomposed by heating with 20 c.c. of concentrated sulphuric acid, 5 grs. of potassium sulphate, and 1 gr. of mercury, according to Kjeldahl's method (*q.v.*, p. 135).

In the combustion of coal the nitrogenous compounds are decomposed with liberation of nitrogen, but in the process of *dry distillation* part of the nitrogen is expelled in a combined form, chiefly as ammonia, together with small quantities of hydrocyanic acid, cyanogen, pyridine, and other organic nitrogenous compounds. The combined nitrogen in coal generally amounts to 1 to 2 per cent., but less than half of this remains in combination after the distillation.

The ammonia recovered in gasworks and coking plants, which comes on the market chiefly in the form of ammonium sulphate, is a valuable by-product, largely used as a fertilizer.

7. Calculation of the Calorific Value by Dulong's Formula.—The amount of heat evolved in the complete combustion of 1 kilogram of fuel, expressed in calories, is termed the "fuel value" or "calorific power." This value is most accurately determined by burning a sample of the fuel in a calorimeter. The experimental determination, however, is laborious; hence, in technical practice, it is usual to calculate the calorific value approximately from the ultimate analysis by Dulong's method. This is done by adding together the heats of combustion of the carbon, sulphur, and *part* of the hydrogen. It is assumed that the oxygen present in coal is already combined with hydrogen as water. Since these elements are united in the ratio of 8:1, 1 part of hydrogen is deducted for every 8 parts of oxygen found (or one-eighth of the oxygen percentage from the amount of hydrogen), the heat of combustion of the residual hydrogen then being brought into the calculation.

This method of calculation is, of course, not strictly accurate, since the carbon in coal exists, not in the elemental form, but in obscure combinations with hydrogen and oxygen. Nevertheless, the values calculated from Dulong's formula agree so well with those obtained by the calorimetric method that they may be taken as sufficiently accurate for commercial purposes.

The following "Heats of Combustion" are required for working out the formula:

(1) $C+O_2=CO_2+97{\cdot}7$ Cals.
(2) $S+O_2=SO_2+71{\cdot}0$ Cals.
(3) *a*. $H_2+O=H_2O$ (liquid) $+68{\cdot}4$ Cals.
b. $H_2+O=H_2O$ (steam) $+57{\cdot}6$ Cals.

From these molecular heats of combustion we find that—

1 k. gr. carbon yields on combustion $\frac{97{\cdot}7\times1{,}000}{12}=8{,}140$ Cals.

1 ,, sulphur ,, ,, $\frac{71{\cdot}0\times1{,}000}{32}=2{,}210$,,

1 ,, hydrogen ,, ,, $\frac{68{\cdot}4\times1{,}000}{2}=34{,}200$,,

Suppose the analysis has given—

c per cent. carbon, *h* per cent. hydrogen, *n* per cent. oxygen and *s* per cent. sulphur.

Assuming that the water vapour produced in the combustion condenses to the liquid state, the calorific value of 1 kilogram of coal will be—

$$\left[81{\cdot}4c+342\left(h-\frac{n}{8}\right)+22{\cdot}1s\right]\text{ Calories.}$$

Generally, however, it is assumed that the water remains in the form of steam, in which case the effective heat of combustion of 1 kilogram of hydrogen is only $\frac{57{\cdot}6\times1{,}000}{2}=28{,}800$ Calories and the calorific value of the coal is correspondingly lower. Further, the amount of heat required to convert into steam any moisture present in the coal must be deducted. The latent heat of evaporation of a gram-molecule of water is represented by the difference of equations 3*a* and 3*b*—*i.e.*, $68{\cdot}4-57{\cdot}6=10{\cdot}8$ Calories. Hence, if the coal contains w per cent. of moisture, determined by (1), p. 15,

$$\frac{10{\cdot}8\times1{,}000}{18}\times\frac{w}{100}=6{\cdot}0\times w\text{ Calories,}$$

must be deducted from the calorific value.

The complete formula is thus:

Calorific value per kilogram=

$$=\left[81{\cdot}4c+288\left(h-\frac{n}{8}\right)+22{\cdot}1s-6{\cdot}0w\right]\text{ Calories.}$$

Example : The analysis of a coal gave—

Carbon	81·9	per cent.
Hydrogen	5·1	,,
Nitrogen	1·3	,,
Sulphur	0·9	,,
Water	1·4	,,
Ash	3·1	,,
	93·7	,,

The difference 100 – 93·7=6·3 per cent. is taken as oxgyen. Calorific value

$$=(81{\cdot}4\times81{\cdot}9)+288\left(5{\cdot}1-\frac{6{\cdot}3}{8}\right)+(22{\cdot}1\times0{\cdot}9)-(6{\cdot}0\times1{\cdot}4)$$

$$=7{,}931\text{ Calories per kilogram.}$$

Fuels may be solid, liquid, or gaseous in form. The natural solid fuels include wood, peat, lignite, coal, and anthracite, all of which are derived primarily from cellulose. Cellulose $n(C_6H_{10}O_5)$ is the principal constituent of plant fibre. It is formed in the living plant from water and atmospheric carbon dioxide, with elimination of oxygen. This vital process takes place under the influence of sunlight and is accompanied by the absorption of radiant energy. In the combustion of woody fibre the process is reversed; oxygen is taken up to produce carbon dioxide and water, the latent energy becoming available in the form of heat.

Wood, especially wood-charcoal, is sometimes employed where fuel free from sulphur and ash is required—*e.g.*, in the melting of glass and the firing of porcelain; also, in Russia and Scandinavia, for the smelting of iron ores. The calorific value of the air-dried material is about 3,500 Cals.

Peat consists of the partially decayed débris of the lower forms of vegetation. It contains a high percentage of water, which is very difficult to remove. For this reason, and also on account of its low density and calorific power (3,000 to 4,000 Cals.), air-dried peat is at present of little importance as a fuel.

Lignites are intermediate in character between peat and coal, varying from fibrous deposits, retaining their original structure, to compact masses of brown coal. Since the process of decomposition is less advanced than in black coal, the lignites contain more vegetable matter and, particularly, a much higher percentage of oxygen. The amount of moisture present is usually high. On the Continent large quantities of brown coal are made into briquettes for domestic use. For this purpose the moisture content is first reduced to about 15 per cent., after which the material is submitted to a pressure of 1,000 to 1,500 atmospheres, the resinous constituents cementing the coal firmly together without the addition of other binding substances.

Coal is by far the most important fuel. The calorific power of bituminous coal ranges from 7,000 to 8,000 Calories, while that of the best anthracite—the oldest variety of coal, which consists almost entirely of carbon—approaches 9,000 Calories.

Coal is usually treated before it appears in the market. It is sorted into various sizes by passing over graduated screens. The smaller grades are generally washed to reduce the amount of ash, and sulphur derived from pyrites.

For the manufacture of briquettes from small coal binding substances are required, such as asphalt, pitch, or sulphite cellulose.

The dry distillation of coal serves on the one hand for the manufacture of illuminating gas and by-products such as ammonia and tar, and for the production of the hard, dense coke required in metallurgical operations.

In England and Sweden anthracite is frequently employed in blast furnaces without preliminary treatment.

Liquid Fuels.—The most important of these are the distilled mineral oils, such as petrol, benzene and kerosene, and alcohol, which are largely used in internal combustion engines and for domestic purposes. Heavy petroleum oils and tar oils are also employed in engines of the Diesel type. The crude petroleum residues known as "masut," which are obtained in enormous quantities from the refineries at Baku, have long been utilized as fuel for locomotives on the railways of Southern Russia and steamers on the Volga and the Caspian Sea.

Gaseous Fuels.—Natural gas, consisting chiefly of methane, is obtained in the vicinity of oil-wells in North America and around Baku, and is of considerable local value.

Of great commercial importance are the gaseous fuels prepared by the action of steam or air, or a mixture of steam and air, on carbonaceous substances.

Gas firing possesses notable advantages over direct firing with coal and coke. Solid fuels require, in practice, a large excess of air for complete combustion, while for gas firing slightly more than the theoretical amount is sufficient; consequently, in the latter case less heat is carried away in the waste gases. Secondly, the fuel gases can be preheated on the regenerative system, thus enabling higher temperatures to be obtained. Gas firing also allows more uniform heating and better control of the temperature. A further advantage is that the gas can be freed from impurities before use.

The combustible gases obtained by the partial oxidation of carbonaceous substances in "producers" are given the general name of "producer gas." Their composition will obviously depend upon the nature of the reacting substances. By the action of air on coke, under producer conditions, a mixture consisting mainly of carbon monoxide diluted with nitrogen is obtained. When coal is employed, the resulting gas contains methane and other hydrocarbons. By the interaction of steam and carbon a mixture of carbon monoxide and hydrogen is produced. Other mixtures are formed by the joint action of air and steam on carbon. The principal varieties of producer gas are air gas, water gas, and semi-water gas or mixed gas.

(1) *Air gas* is produced by passing a limited amount of air through incandescent carbon in a generator—a high shaft furnace constructed of firebrick. The primary air is admitted through a grating at the bottom of the generator. Near the intake the carbon burns to carbon dioxide, which, however, on passing through the upper layers of highly heated carbon, is reduced to carbon monoxide, according to the equation

$$CO_2 + C = 2CO.$$

Since every molecule of oxygen yields two molecules of carbon monoxide, the producer gas thus formed contains, under ideal conditions, 2×20 volumes of carbon monoxide and 79·2 volumes of nitrogen, or 34·4 per cent. of carbon monoxide and 65·6 per cent of nitrogen.

The reaction is exothermic. Carbon burning to carbon monoxide furnishes 29·3 Cals., carbon monoxide burning to carbon dioxide 68·4 Cals.; hence about 30 per cent. of the calorific power of the coal is set free in the generator and is not available in the subsequent combustion.

Much of the heat thus liberated in the generator can, however, be recovered either by building the producer plant close to the furnace, so that the hot gases are used before they have time to cool, or by preheating the secondary air (*i.e.*, the air supplied for the burning of the producer gas within the furnace) with waste heat from the flue gases. This may be done either by the *regenerative* system of Siemens or the *recuperative* method. The regenerators consist of long chambers packed with a chequer-work of firebricks, through which the hot waste gases and the secondary air (or fuel gas if necessary) are passed alternately. The regenerative method gives excellent results, but its intermittent action is a disadvantage. For this reason the more convenient continuous recuperators are generally employed, especially in the manufacture of illuminating gas. In the recuperator the hot waste gases and the air to be heated are passed counterwise through parallel flues separated only by a thin wall of refractory material.

(2) *Water gas* is prepared by the action of steam on carbon at high temperatures. Coke, or anthracite, is heated to incandescence by an air-blast. The air is then shut off and a current

of steam is passed through the glowing mass in the generator. The following reactions take place:

$$C + H_2O = CO + H_2 - 28{\cdot}3 \text{ Cals.}$$
$$C + 2H_2O = CO_2 + 2H_2 - 19{\cdot}0 \text{ Cals.}$$

Since both these reactions are strongly endothermic, the temperature of the mass falls rapidly, and the production of carbon dioxide becomes more marked. It is then necessary to cut off the supply of steam and to heat up the producer again with air. The process is thus intermittent, the "hot-blow" or air-blast alternating with the "cold-blow" or steam injection. In the old form of generator "air gas" alone was produced during the hot-blast period ($2C + O_2 = 2CO + 29{\cdot}3$ Cals.) and this was used to generate steam for the "run." In modern practice, however, the fuel consumed during the blow is burnt to carbon dioxide ($C + O_2 = CO_2 + 97{\cdot}7$ Cals.), the large amount of heat developed in this reaction quickly raising the mass to the required temperature. Thus, in the Dellwik-Fleischer plant a shallow layer of coke is rapidly oxidized with a powerful blast of air. By this means the duration of the "hot-blow" is shortened, and that of the "run" proportionally increased.

(3) *Dowson gas* consists of a mixture of air gas and water gas, and is produced by the simultaneous action of air and steam on incandescent carbonaceous material. The proportion of air to steam is regulated in such a way that the heat absorbed in the decomposition of steam (28·3 Cals.) is exactly balanced by that liberated in the air-carbon reaction, so that the high temperature of the burning mass is maintained.

Dowson gas is also known under the names of power gas, mixed gas, or suction gas.

2. DRINKING-WATER AND WATER FOR INDUSTRIAL PURPOSES.

A.—Full Chemical Analysis.

THE water submitted to analysis must be perfectly clear. Turbid water should be filtered before use.

1. Determination of Total Solids.—300 to 1,000 c.c. of the water are evaporated to dryness (on a water-bath) in a weighed platinum dish protected from dust by a large inverted funnel suspended a few inches above it. When evaporation is complete, the dish is heated in a drying-oven at 110° for two hours, cooled in a desiccator, and weighed as rapidly as possible, since the residue is usually hygroscopic.

To find whether organic matter is present and to obtain some indication of its amount, the dish containing the residue is placed on a triangle and gradually heated to dull redness over a naked flame. When the amount of organic substance is small, a brown coloration is produced, which quickly disappears. If, during the ignition, the residue shows black patches which are only removed by prolonged heating, a large amount of organic matter is indicated. Very large amounts cause blackening of the whole mass to such an extent that it is frequently impossible to obtain a pure white residue even after prolonged ignition. Organic impurities of vegetable origin generally give a faint characteristic odour on heating, while animal nitrogenous substances produce a smell resembling that of burning hair or feathers.

Sometimes the residue is dried at 140° or 180° C., since at the lower temperature many salts still retain their water of crystallization; there is, however, a danger of certain substances, especially organic matter, undergoing decomposition at the higher temperature. As the experiment is only intended to furnish information of a general character, the temperature selected is of little importance, provided the determination is always done under exactly the same conditions, so that the results obtained from various kinds of water are comparable.

2. Determination of the Reducing Capacity.—100 c.c. of the water are measured into an Erlenmeyer flask of about 300 c.c. capacity and mixed with 10 c.c. of a centinormal solution of *alkaline* potassium permanganate (containing 20 grs. of pure sodium hydroxide per litre). The liquid is boiled for ten minutes and, after allowing it to cool slightly, 10 c.c. of dilute sulphuric acid and 10 c.c. of centinormal oxalic acid are added and the mixture shaken until the colour has completely disappeared. The centinormal permanganate solution is then run in from a burette until a faint permanent red tint is obtained. This is most easily observed by holding the flask over a sheet of white paper or opal glass during the titration.

In calculating the amount of oxygen consumed by the organic matter, 0·2 c.c. of permanganate solution should be deducted for the loss of oxygen during the initial boiling; also, if any considerable amount of ferrous salts is found to be present on subsequent analysis, a corresponding correction is required.

Should 100 c.c. of the sample reduce more than 5 c.c. of the centinormal permanganate solution, a smaller volume is taken and diluted with pure water.

The result is expressed in milligrams of oxygen consumed by 1 litre of water. In the case of drinking-water this should not exceed 2 to 3 milligrams.

Since the various organic substances in water cannot be separately determined, the above indirect method is used to estimate approximately the total amount of organic matter present.

3. Estimation of Dissolved Oxygen.—A 250 c.c. flask provided with a well-fitting glass stopper is filled with distilled water and its *full capacity* accurately determined by weighing. It is then filled with the water under examination, introduced through a long, narrow tube reaching to the bottom of the flask, and allowed to overflow for a few minutes; 1 c.c. of a solution of potassium iodide in caustic potash and then 1 c.c. of manganous chloride solution (*vide infra*) are added from a pipette having a long stem, which is thrust deeply into the water. After inserting the stopper and seeing that no air is left in the neck, the flask is well shaken and allowed to stand for a few minutes until the precipitate has subsided. About 5 c.c. of concentrated hydrochloric acid are added, as before from a long-stemmed pipette, and the flask again shaken, whereupon the precipitate dissolves with separation of iodine, which is then titrated with a centinormal solution of thiosulphate.

The iodide solution is prepared by dissolving one part of the purest potassium hydroxide (free from nitrite) in two parts of distilled water, and adding 5 grs. of potassium iodide for every 50 c.c. The manganous chloride solution consists of 40 grs. of pure crystalline $MnCl_2.4H_2O$ (free from iron) in 100 c.c. of water.

The manganous hydroxide precipitated by the addition of caustic potash to manganous chloride absorbs the dissolved oxygen, passing into manganic hydroxide (or other higher oxide of manganese) according to the equation—

$$4Mn(OH)_2 + O_2 + 2H_2O = 4Mn(OH)_3.$$

On adding hydrochloric acid the following reaction takes place:

$$2Mn(OH)_3 + 6HCl + 2KI = 2MnCl_2 + 2KCl + I_2 + 6H_2O.$$

The amount of iodine liberated from the potassium iodide is equivalent to the oxygen absorbed.

Good drinking-water should always contain oxygen in solution. Water at 15° C. saturated with air at atmospheric pressure contains about 7 c.c. of dissolved oxygen per litre. Deficiency of oxygen indicates the presence of decomposing organic matter, by which is it absorbed.

4. Determination of Carbonic Acid—(*a*) *Free Carbonic Acid.*—A 100 c.c. graduated flask, having the mark fairly low on the neck, is filled with the sample as described in the preceding experiment.

The water above the mark is then removed by means of a pipette. After adding a few drops of phenolphthaleïn, the sample is titrated with a centinormal solution of sodium carbonate until a faint red coloration is obtained, which persists for at least five minutes with the flask inverted.

(*b*) *Fixed Carbonic Acid.*—100 c.c. of water are titrated with centinormal hydrochloric acid, using methyl orange as indicator.

Fresh well-water and spring-water almost invariably contain a small amount of free carbonic acid, giving a slightly acidic indication with phenolphthaleïn. With methyl orange, however, the natural waters show an alkaline reaction until the whole of the bicarbonate has been decomposed by the hydrochloric acid used in the titration, and a slight excess of the mineral acid is present:

$$Ca(HCO_3)_2 + 2HCl = CaCl_2 + 2H_2O + CO_2.$$

Artificially softened water (*vide infra*) generally contains some free lime or soda, and for this reason gives an alkaline reaction with phenolphthaleïn.

The method of determining free carbonic acid described under (*a*) gives only approximate results, but in most cases these are sufficiently accurate for technical work. During the titration the following reaction takes place:

$$H_2CO_3 + Na_2CO_3 = 2NaHCO_3.$$

It is assumed that the sodium bicarbonate thus formed is neutral to phenolphthaleïn; this, however, is true only for concentrated solutions at temperatures slightly above zero.

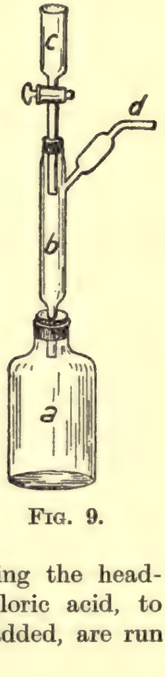


FIG. 9.

When an accurate determination of the free carbonic acid is required, it is best to ascertain first of all the total carbonic acid present and then to deduct the fixed carbonic acid already found in (*b*). For this purpose the apparatus shown in Fig. 9 may be used. The capacity of the bottle *a* is ascertained by charging it with distilled water to a mark about half-way up the neck; 20 grs. of metallic zinc, previously freed from carbonate by washing with dilute hydrochloric acid followed by distilled water, are placed in the empty bottle, which is then filled up with the test-water and closed by means of a tightly fitting rubber stopper carrying the head-piece *b*. Then 50 c.c. of concentrated hydrochloric acid, to which a drop of " platinic chloride " has been added, are run in very gradually from the funnel *c*, this operation extending over about an hour. The hydrogen evolved in *a* displaces and carries over the whole of the carbon dioxide. The gases are led first through a tube of calcium chloride attached to *d* and then through a weighed tube of soda lime. At the end of the experiment the hydrogen is swept out of the soda-lime tube by a current of dry air free from carbon dioxide. The gain in weight corresponds to the total carbonic acid originally in the sample.

When free carbonic acid is present, the calcium salt must exist in the form of bicarbonate; hence in this case the " fixed carbonic acid " is identical with " bicarbonate carbonic acid." Thus, the titration with methyl orange indicates simultaneously the amount of bicarbonates present. It is assumed that no considerable amount of salts of other weak acids, such as silicates or borates, is present; these are exceptional, and are readily detected.

5. Determination of Sulphates.—250 to 1,000 c.c. of the filtered water are slightly acidified with hydrochloric acid and evaporated to about 200 c.c. The sulphates are then precipitated with barium chloride in the usual way. Waters containing much iron should first be treated with ammonia and filtered.

6. Determination of Chlorine.—250 to 1,000 c.c. of the water are acidified with dilute nitric acid and evaporated down to about 200 c.c. An excess of decinormal silver nitrate solution is added, and then titrated back with decinormal ammonium thiocyanate.

Any large amount of organic matter should first be removed. For this purpose the water is heated to boiling, and permanganate solution added until a faint coloration is obtained which does not disappear after boiling for five minutes; the excess of permanganate is then reduced with a very dilute solution of ferrous sulphate added drop by drop.

If the sample contains more than 20 to 30 milligrams of chlorine per litre, pollution with sewage or domestic refuse may be suspected. Such water should not be used for drinking, except where the chlorine is known to have been derived from salts naturally present in the soil, in which case a considerably larger amount is permissible. A high percentage of chlorides in industrial water is also undesirable, on account of their corrosive action, which is aided by the presence of dissolved oxygen. Magnesium chloride especially is highly deleterious, owing to the fact that it undergoes hydrolytic dissociation at the boiling-point of water, with liberation of hydrochloric acid. Waters containing this salt should not be used for steam-raising.

7. Estimation of Nitrates—(*a*) *Qualitative.*—2 c.c. of the water to be examined are carefully mixed with about three times this volume of concentrated sulphuric acid, and allowed to cool completely. Then about 1 c.c. of a solution of 0·1 gr. of brucine in 50 grs. of concentrated sulphuric acid is added. The presence of nitric acid is indicated by a red coloration, which changes quickly to orange and ultimately to yellow. The depth of colour gives an indication of the amount of nitric acid present. According to L. Winkler, the following tints are observed:

When 1 litre of water contains 100 mgr. N_2O_5, cherry red, rapidly changing to orange and becoming yellow on long standing.

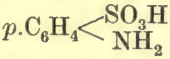
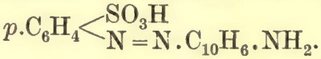
When 1 litre of water contains 10 mgr. N_2O_5, rose red, becoming pale yellow on long standing.

When 1 litre of water contains 1 mgr. N_2O_5, pale rose red, becoming almost colourless on standing.

Brucine $(C_{23}H_{26}N_2O_4)_n$ is a highly poisonous alkaloid of unknown constitution extracted from *nux vomica*. It is the most reliable reagent for the detection of traces of nitric acid in presence of nitrous acid. Any nitrous acid contained in the water is absorbed by the excess of concentrated sulphuric acid, forming nitroso-sulphuric acid, which in the cold does not react with brucine.

(*b*) *Quantitative.*—A quantitative determination is only necessary when the preliminary qualitative test indicates the presence of a considerable amount of nitric acid; 1 litre of water is evaporated, with the addition of a little pure caustic potash, to about 150 c.c. and the nitrate is determined by Devarda's method (p. 90).

8. Determination of Nitrites—(*a*) *Qualitative.*—20 c.c. of the water are mixed in a test-tube with 2 to 3 c.c. of an acetic acid solution of *a*-naphthylamine-sulphanilic acid. The tube is loosely plugged with a cork and heated to 70° to 80° C. by immersion in a water-bath. The merest trace of nitrous acid produces almost immediately a distinct red coloration. With 0·001 milligram of nitrous acid per litre the colour appears in one minute. The reagent is prepared in the following way: 0·5 gr. of sulphanilic acid is dissolved in 150 c.c. of 30 per cent. acetic acid; 0·1 gr. of *a*-naphthylamine is boiled with 20 c.c. of water, the residue filtered off and the filtrate acidified with 150 c.c. of 30 per cent. acid. The two solutions are then mixed together and preserved in a well-stoppered bottle. Should the stock solution gradually assume a reddish colour (due to the action of atmospheric air), it may be shaken with a little zinc dust and filtered.

The above test depends upon the formation of a vivid red dye. By the action of nitrous acid, sulphanilic acid  $p.\mathrm{C_6H_4}{<}\begin{array}{l}\mathrm{SO_3H}\\ \mathrm{NH_2}\end{array}$ is diazotized, and combines with *a*-naphthylamine ($\mathrm{C_{10}H_7.NH_2}$) to form the azo colour  $p.\mathrm{C_6H_4}{<}\begin{array}{l}\mathrm{SO_3H}\\ \mathrm{N=N.C_{10}H_6.NH_2}\end{array}$.

9. Determination of Ammonia—(*a*) *Qualitative.*—Measure out 50 c.c. of the water into a glass cylinder. Add about 1 c.c. of a solution of 25 grs. of Rochelle salt in 50 c.c. of water and 1 c.c. of Nessler's reagent (*vide infra*). Place the vessel upon a sheet of white paper and observe the colour; 0·05 milligram of ammonia per litre produces a yellow coloration, while larger amounts give a brown coloration and finally a precipitate. The sample of water, if not perfectly clear and colourless, should be distilled in the following manner: The apparatus is first freed from any trace of ammonia by placing 500 c.c. of pure water, together with about 1 c.c. of a saturated solution of caustic soda, in the retort and distilling it through the condenser until 50 c.c of the distillate, tested as above with Nessler's reagent, show no coloration even after standing for a quarter of an hour. After emptying the retort, 500 c.c. of the sample are introduced and distilled as before with caustic soda. The first 50 c.c. of the distillate are taken for the test.

Nessler's reagent is prepared in the following way: Triturate about 5 grs. of mercuric iodide with a few cubic centimetres of pure water in a small mortar. Wash into a flask. Add 2·5 grs. of potassium iodide and a cold solution of 10 grs. of caustic soda in the smallest possible quantity of water. Dilute to 50 c.c. with redistilled water. Allow the precipitate to settle, decant the clear solution, and preserve in a well-stoppered bottle, kept in the dark.

(*b*) *Quantitative.*—The above method is also suitable for the quantitative determination of ammonia when this is present only in a small amount. Two glass cylinders similar in all respects, having a capacity of about 150 c.c., and provided with accurately ground stoppers, are required; 100 c.c. of pure distilled water are measured into one of the cylinders, and an equal volume of the sample to be tested —previously distilled as in (*a*)—into the other. When the vessels have acquired a uniform temperature, 2 c.c. of Nessler's reagent are added, drop by drop, to each. Then a solution of ammonium chloride equivalent to 0·1 milligram of ammonia per cubic centimetre is run into the standard water, with constant shaking—an equal volume of pure water being added to the sample—until the tints are exactly alike.

Mercuric iodide dissolves in a solution of potassium iodide, forming a complex K_2HgI_4, which, in the presence of caustic potash, reacts with ammonia according to the equation

$$2K_2HgI_4 + 3KOH + NH_3 = Hg_2(OH)_2NH_2I + H_2O + 7KI,$$

producing a precipitate or strong yellow coloration.

The object of adding Rochelle salt (sodium potassium tartrate) is to prevent precipitation, by the excess of alkali, of any iron or alkaline earths present in the water, which might otherwise interfere with the test. These impurities combine with the tartrate, forming soluble complex salts. Since, however, the tint produced by the interaction of Nessler's reagent and ammonia depends to a certain extent on the amount of alkali salts present, it is always advisable to remove these by distillation before the test is applied.

In water for industrial purposes small amounts of nitrates and the traces of nitrites and ammonia which are occasionally found are of little consequence, but drinking-water should not contain more than 10 to 15 milligrams of nitric acid per litre, while nitrites and ammonia should be completely absent. These nitrogenous compounds, although not of themselves harmful in minute quantities, afford strong evidence of the pollution of water by decomposing organic matter. The presence of nitrous acid is especially significant, since this is a metabolic product of pathogenic bacteria, and water containing it may be very dangerous to health.

10. Determination of Silica, Iron, Alumina, Lime, and Magnesia—(*a*) *Silica.*—1 litre of water is acidified with hydrochloric acid and evaporated, with the addition of 0·2 gr. of potassium chlorate, to dryness on the water-bath. The residue is moistened with a few drops of hydrochloric acid, and again evaporated completely to dryness. This operation is repeated, after which the substance is taken up with hot dilute hydrochloric acid and filtered. The residue is burnt on the filter in a platinum crucible, ignited, and weighed as SiO_2.

If the water originally contained much calcium sulphate, some of this will appear in the silica. When any appreciable amount of insoluble residue is obtained, the silica should be volatilized by gently heating in the crucible with about 1 c.c. of pure hydrofluoric and a few drops of concentrated sulphuric acid. The residue is again ignited and weighed, the difference between the first and second weighings representing silica. The residue remaining in the crucible, consisting of calcium sulphate (and possibly a little iron oxide), is dissolved in concentrated hydrochloric acid, and the solution added to the filtrate.

(*b*) *Iron and Alumina.*—The filtrate from (*a*) is heated to boiling, the iron and aluminium co-precipitated with ammonia, filtered off, ignited and weighed in the crucible containing the residue from the silica determination.

In commercial water analysis the determination of alumina, which is generally unimportant, is often omitted, and the iron determined by the following method:

Iron by Titration.—The filtrate from (*a*) is heated to boiling and the iron and aluminium are precipitated by the addition of ammonium chloride and ammonia. The precipitate is dissolved in dilute sulphuric acid, reduced with zinc or with hydrogen sulphide, and titrated with permanganate. If the amount of iron is very small, more accurate results may be obtained by the following method:

Iron by Colorimetric Method.—50 to 200 c.c. of the sample are boiled with 1 c.c. of pure 30 per cent. nitric acid, evaporated to a small bulk, and washed into a 100 c.c. graduated flask. After cooling, the flask is filled to the mark with distilled water; 5 c.c. of the liquid are pipetted into a graduated cylinder of about 30 c.c. capacity, provided with a glass stopper, and shaken with 5 c.c. of a 10 per cent. solution of ammonium thiocyanate and 10 c.c. of ether until the colour of the aqueous layer, which separates on standing, is quite discharged; 5 c.c. of distilled water containing, like the sample, 1 c.c. of 30 per cent. nitric acid in 100 c.c. are treated in the same way with ammonium thiocyanate and ether. A solution of ferrous ammonium sulphate containing 0·1 gr. Fe per litre is then run in, drop by drop, from a burette (graduated in $\frac{1}{20}$ c.c.), and an equal volume of water added to the test solution until the tints in both cylinders are exactly the same, the contents being well shaken after each addition. The volume of the iron solution required for the titration should not exceed 2 c.c., otherwise the sample of water must be diluted before use. The cylinders are allowed to stand, and any change of colour becoming appreciable after the lapse of a few hours is corrected. The standard iron is prepared by dissolving pure ferrous ammonium sulphate. It is advisable to make a stock solution ten times the required strength with the addition of 5 c.c. of pure sulphuric acid per litre. This is diluted immediately before use, as the weak solution does not keep well.

The iron in ferruginous waters usually occurs as ferrous bicarbonate, $Fe(HCO_3)_2$. Such waters become turbid on exposure to air, owing to the separation of small flocks of ferric hydroxide. While not actually injurious to health, they have an unpleasant astringent taste and are uninviting in appearance. They are unsuitable for use in laundries. Bacteria of the *Crenothrix* type flourish in these waters, occasionally blocking the mains. A maximum of 0·3 milligram of iron per litre is permissible in drinking-water and water for household use, but this amount is excessive in waters intended for the dyeing and paper industries.

(c) *Lime and Magnesia.*—Acidify the filtrate from the iron group with hydrochloric acid and evaporate, if necessary, to a smaller volume. Add oxalic acid. Heat to boiling, and add ammonia, drop by drop (without interrupting the boiling), until the solution is slightly alkaline. Allow to stand for twenty minutes. Filter off the calcium oxalate, dissolve in dilute sulphuric acid, and titrate at 70° C. with standard permanganate solution. Calculate the percentage of lime. Acidify the filtrate slightly with hydrochloric acid, add ammonium phosphate, heat to boiling, mix with a large excess of ammonia, and set aside for several hours. Filter off the precipitate of magnesium ammonium phosphate, wash with a 10 per cent. cold solution of ammonia, ignite, and weigh as $Mg_2P_2O_7$.

In natural waters lime occurs either as bicarbonate or sulphate (gypsum), magnesia usually as bicarbonate, and more rarely as chloride or sulphate. Waters containing appreciable quantities of these salts are said to be "hard," and various degrees of hardness are distinguished according to the amounts present. The English degree of hardness is represented by 1 milligram of $CaCO_3$ in 70 c.c. of water, the French unit by 1 milligram of $CaCO_3$ in 100 c.c. of water, while, in Germany, 1 degree of hardness corresponds to 1 milligram of CaO (or an equivalent amount, 0·714 milligrams, of MgO) in 100 c.c. of water. Waters of less than about 6 English degrees are considered soft. A further distinction is made between *temporary hardness*, or that which disappears on boiling, and *permanent or residual hardness*. For the determination of these, see p. 40. The loss of hardness on boiling is due to the decomposition of the bicarbonates into insoluble neutral carbonates and carbon dioxide:

$$Ca(HCO_3) = CaCO_3 + CO_2 + H_2O.$$

Permanent hardness is due to the small quantities of calcium and magnesium carbonates and the sulphates (especially gypsum) which remain in solution.

Good drinking-water should average about 20 English degrees of total hardness, but 40 degrees is not detrimental. Soft waters, such as rain and glacier waters, are too insipid for drinking.

On the other hand, soft waters are desirable for domestic use. Vegetables, especially peas and beans, do not soften thoroughly on boiling in hard water. The use of hard waters in laundries leads to serious wastage of soap, which is precipitated as an insoluble calcium or magnesium salt. In many industries, such as brewing, tanning, or dyeing, soft water is essential. Hard waters are particularly unsuitable for steam-raising, owing to the fact that the almost insoluble calcium and magnesium salts separate on boiling, forming a hard incrustation on the walls of the boiler, which impedes the conduction of heat and may cause local superheating, with consequent damage to the boiler plates.

For the artificial " softening " of water see below.

11. Determination of Alkalis.—Ignite the residue from determination (1) very gently in a platinum dish. Dissolve in a little dilute hydrochloric acid, add 10 to 15 drops of concentrated sulphuric acid, and take down to dryness. Add a few grains of ammonium carbonate, ignite gently, and weigh.

Calculate the amounts of lime and magnesia found in (*c*) into sulphates, add the amounts of silica, ferric oxide and alumina found in (*a*) and (*b*), and deduct the total from the residue obtained above. The remainder is taken as sodium sulphate. Calculate this to grams of sodium oxide.

The amount of alkalis in natural waters is usually very small, and sodium almost invariably predominates to such an extent that the separate determination of potash is unnecessary. The above method is sufficiently accurate for practical purposes.

The alkali content can also be calculated approximately in the following way: The amounts of all the bases and acids determined are divided by their equivalent weights. The difference between the equivalents of acids and bases must correspond to the amount of alkalis present, provided everything else has been determined. In making the calculation, only the most important constituents are taken into account. Suppose that 1 litre of water is found on analysis to contain—

Acids	65·3	mgr.	fixed CO_2
	29·1	,,	SO_3
	2·1	,,	N_2O_5
	3·1	,,	Cl
Bases	73·2	mgr.	CaO
	18·3	,,	MgO

The equivalents of the acids and bases are thus—

$$\text{Acids} \quad .. \quad .. \quad \begin{cases} \dfrac{65\cdot3}{\frac{1}{2}CO_2} = 2\cdot97 \text{ mgr. } CO_2 \\ \dfrac{29\cdot1}{\frac{1}{2}SO_3} = 0\cdot73 \quad ,, \quad SO_3 \\ \dfrac{2\cdot1}{\frac{1}{2}N_2O_5} = 0\cdot04 \quad ,, \quad N_2O_5 \\ \dfrac{3\cdot1}{Cl} = 0\cdot09 \quad ,, \quad Cl \end{cases}$$

$$\text{Total} = 3\cdot83 \text{ mgr.}$$

$$\text{Bases} \quad .. \quad .. \quad \begin{cases} \dfrac{73\cdot2}{\frac{1}{2}CaO} = 2\cdot61 \text{ mgr. } CaO \\ \dfrac{18\cdot3}{\frac{1}{2}MgO} = 0\cdot92 \quad ,, \quad MgO \end{cases}$$

$$\text{Total} = 3\cdot53 \text{ mgr.}$$

The difference between the acidic and basic equivalents, $3\cdot83 - 3\cdot53 = 0\cdot30$, multiplied by the equivalent weight of sodium oxide $\frac{Na_2O}{2} = 31$, gives the amount of alkalis present in terms of Na_2O—*i.e.*, $0\cdot3 \times 31 = 9\cdot3$ milligrams Na_2O per litre. The suitability of water for drinking purposes cannot be determined by chemical analysis alone; much depends on its physical properties—viz., transparency, colour, odour and taste—and its condition as revealed by microscopic and bacteriological examination. The locality in which it is collected should also be carefully inspected.

As already indicated, the requirements of the various industries differ greatly, and it is seldom possible to find in any one locality water suitable for all purposes.

Waters obtained from springs in mountainous districts usually possess all the properties of good drinking-water, and surface waters collected at a distance from dwellings may generally be used without purification. Where these contain much iron they are purified by exposure to a current of air in a specially constructed apparatus, whereby the ferrous bicarbonate is oxidized to ferric hydroxide which separates out.

Many large towns are dependent upon river-water. To make this wholesome it is filtered through beds of gravel and sand, which retain most, if not all, of the bacteria, provided the flow of water through the filter is not too rapid.

The purification of water for boilers extends only to the removal of the scale producers—viz., lime and magnesia. By the addition of lime-water, the bicarbonates of calcium and magnesium are converted into normal carbonates, according to the equation—

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

The normal carbonate of calcium, being practically insoluble, is readily removed. With magnesium the conditions are complicated by the fact that the normal carbonate is fairly soluble, while the hydroxide is almost insoluble. For this reason 2 molecules of calcium hydroxide must be added to every molecule of magnesium bicarbonate, whereby the latter is converted first into normal carbonate and then into hydroxide, according to the equations—

$$Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 + CaCO_3 + 2H_2O$$

and

$$MgCO_3 + Ca(OH)_2 = Mg(OH)_2 + CaCO_3.$$

Sodium carbonate is then added to remove the gypsum, the following reaction taking place:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

Water containing gypsum and bicarbonates in equal proportions, or in which the former preponderates, is best treated directly with caustic soda, or with a mixture of sodium carbonate and caustic soda, instead of successively with lime and sodium carbonate. By the interaction of caustic soda and calcium bicarbonate, sodium carbonate is produced—

$$Ca(HCO_3)_2 + 2NaOH = CaCO_3 + Na_2CO_3 + 2H_2O,$$

which then reacts with an equivalent amount of calcium sulphate.

All these reactions take place slowly at the extreme dilution and low temperature prevailing; hence the water should remain in contact with the precipitants for several hours before being filtered. The quantities of " softeners " required are calculated from the chemical analysis and the addition is carefully regulated, to ensure complete precipitation of the impurities while avoiding any excess of the reagents. Even after the most careful purification water still retains from 2 to 2·5 degrees of hardness, corresponding to the solubility of $CaCO_3$ and $Mg(OH)_2$, which in each case, at ordinary temperatures, amounts to about 1 degree.

Sometimes the hardness due to gypsum is removed by the addition of barium carbonate in the form of a paste; an excess of this reagent is of little consequence, since it is insoluble. A water-purifier recently placed on the market under the name of Permutit consists of an artificially prepared sodium aluminium silicate, which, although itself insoluble, possesses the property of absorbing from aqueous solutions basic compounds of calcium, magnesium, iron and manganese, giving up its sodium in exchange. This property is utilized for the purification of water, which is run slowly through a cylinder packed with small fragments of Permutit. The exhausted Permutit can be regenerated by digestion with a concentrated solution of common salt, whereby it is reconverted into the original sodium compound.

B.—Abbreviated Analysis.

1. Pfeifer-Wartha Method—(*a*) *Bicarbonate.*—100 c.c. of the water are titrated as described under "Fixed Carbonic Acid" (p. 29) with centinormal hydrochloric acid, using methyl orange as indicator. Since 1 c.c. of acid of this concentration corresponds to 2·8 milligrams CaO, the number of cubic centimetres used multiplied by 2·8* gives the degree of hardness due to bicarbonate, which Pfeifer identifies with temporary hardness.

(*b*) *Total Hardness.*—The titrated sample from (*a*) is mixed with an excess of a solution consisting of equal volumes of decinormal caustic soda and decinormal sodium carbonate, boiled for a few minutes, washed into a 200 c.c. flask, cooled and filled up to the mark; 100 c.c. are passed through a *dry* filter, and the excess of alkali titrated back with decinormal hydrochloric acid, using methyl orange as indicator. The amount of alkali consumed (calculated for 200 c.c. of filtrate) multiplied by 2·8* gives the total hardness. By deducting from this the temporary hardness found in (*a*), the permanent hardness is obtained.

It occasionally happens that less alkali is required in (*b*) than acid in (*a*)—*i.e.*, that the temporary hardness determined in this way exceeds the total hardness. Obviously this can only be the case when the water contains alkali bicarbonate—*i.e.*, $NaHCO_3$. According to Pfeifer, such waters are frequently met with in the Hungarian Plain. The amount of sodium bicarbonate present corresponds to the difference *a*-*b*.

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* To express in English degrees, multiply by 3·5 instead of 2·8.

(*c*) *Magnesia.*—100 c.c. of the sample are mixed in a 200 c.c. flask with a measured volume of decinormal hydrochloric acid, slightly in excess of that required in titration (*a*), and boiled for a few minutes to expel the carbonic acid. After adding 25 to 50 c.c. of clear lime-water, the mixture is allowed to cool and diluted to the mark with cold, freshly distilled water; 100 c.c. of the filtrate are titrated with decinormal hydrochloric acid for the excess of calcium hydroxide. The concentration of the lime-water used is then determined exactly by making a blank experiment in the same way.

From the total lime-water consumed an amount is deducted corresponding to the excess of hydrochloric acid, and the remainder calculated into terms of magnesia. The latter is precipitated according to the equation—

$$Ca(OH)_2 + MgCl_2 = Mg(OH)_2 + CaCl_2;$$

hence 1 c.c. of decinormal lime-water is equivalent to 1 c.c. of decinormal MgO. By multiplying the number of cubic centimetres of decinormal lime-water used by 2·8,* the degree of hardness due to magnesia is obtained.

This abbreviated method is based upon the assumption that in the titration (*a*) hydrochloric acid is consumed solely by the bicarbonates of calcium and magnesium. As a rule, this assumption holds good for natural waters (the Hungarian waters containing soda have already been cited as an exception). The three determinations (*a*), (*b*) and (*c*) thus furnish sufficient data for the calculation of the quantities of lime and sodium carbonate required in the purification of the water.

If H_t denote the temporary hardness found from (*a*) and H_{mg} the hardness due to magnesia found from (*c*), the amount of lime required for 100 litres of water is

$$(H_t + H_{mg}) \text{ grs. CaO} \ldots\ldots\ldots \text{(i)},$$

since H_t represents the number of milligrams of CaO plus the equivalent amount of MgO in the form of bicarbonate present in 100 c.c. of water. Every milligram of CaO requires for its precipitation an equal amount of lime, but the MgO equivalent to 1 milligram CaO requires, as already explained, twice this amount of lime; hence H_{mg} milligrams CaO must still be added. Calculating for 100 litres instead of 100 c.c., the weight of CaO in (i) is expressed in grams in place of milligrams.

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* See note opposite.

Again, the permanent hardness indicates how much calcium is present as sulphate (more rarely as chloride). This is precipitated with sodium carbonate of which 1 molecule is required for every molecule of CaO combined as sulphate. The ratio of the molecular weights of CaO and Na_2CO_3 is 56 : 106 or 1 : 1·89; hence 100 litres of water will require

$$1{\cdot}89 \times H_p \text{ grs. } Na_2CO_3 \ldots\ldots\ldots \text{(ii)},$$

where H_p denotes the permanent hardness obtained by deducting the temporary hardness from the total hardness.

Example: 100 litres of water having a temporary hardness $=11{\cdot}2$ degrees, a magnesia hardness $=3{\cdot}0$ degrees, and a permanent hardness $=6{\cdot}4$ degrees will require for its purification—

$$11{\cdot}2+3{\cdot}0=14{\cdot}2 \text{ grs. CaO},$$
$$1{\cdot}89\times 6{\cdot}4=12{\cdot}1 \text{ grs. } Na_2CO_3.$$

2. Clark's Method—*Estimation of the Total Hardness by Means of Soap Solution.*—The soap solution is prepared by dissolving 10 grs. of potassium oleate in 500 c.c. of alcohol (56 per cent. by volume). Any insoluble residue is filtered off. The soap solution is standardized with one of barium chloride containing 0·523 gr. of $BaCl_2.2H_2O$ per litre; 100 c.c. of the barium chloride solution are placed in a stoppered bottle of about 200 c.c. capacity, and the soap solution added slowly from a burette. After each addition the bottle is shaken vigorously. The test is finished when the thick lather formed on the surface persists for at least five minutes without breaking, with the bottle resting on its side. The soap solution is then diluted with "56 per cent." alcohol until 45 c.c. exactly correspond to 100 c.c. of the barium chloride solution.

In determining the hardness of water the test is performed in exactly the same way. In the case of soft water 100 c.c. of the sample are taken, for hard waters only 50 or 25 c.c., which are diluted with distilled water to 100 c.c. before use. Since the amount of soap solution required does not increase strictly in proportion to the hardness of the water, the following empirical table is employed:

Table of Hardness for Use with Clark's Method.

C.c. of Soap Solution required.	*Degrees of Hardness.*	
3·4	0·5	1 c.c. soap = 0·25°
5·4	1·0	
7·4	1·5	
9·4	2·0	
11·3	2·5	1 c.c. soap = 0·26°
13·2	3·0	
15·1	3·5	
17·0	4·0	
18·9	4·5	
20·8	5·0	
22·6	5·5	1 c.c. soap = 0·277°
24·4	6·0	
26·2	6·5	
28·0	7·0	
29·8	7·5	
31·6	8·0	
33·3	8·5	1 c.c. soap = 0·294°
35·0	9·0	
36·7	9·5	
38·4	10·0	
40·1	10·5	
41·8	11·0	
43·4	11·5	1 c.c. soap = 0·31°
45·0	12·0	

The soap test, on account of its simplicity, is extensively employed in practice. A solution of soap—*i.e.*, the sodium or potassium salt of fatty acids—froths readily on agitation, but when it is mixed with water containing lime and magnesia the corresponding calcium or magnesium salts of the fatty acids are precipitated, and frothing only begins after the precipitation is complete. The method is inapplicable to waters containing much magnesia, owing to the difficulty, in this case, of determining the end-point with precision.

3. COAL GAS.

1. Volumetric Analysis (Hempel's Method).

THE apparatus used for the volumetric analysis of gases is shown in the accompanying diagram. The gas is enclosed in a burette (Fig. 10), which is connected by means of a rubber tube, about 1 metre in length, with a levelling vessel. The reagents used for absorbing the different constituents of gaseous mixtures are contained in bulb pipettes mounted on stands (Figs. 12, 13 and 14). The apparatus is used in the following way: The liquid is brought to the same level in both limbs and the volume of gas read off. The burette is then connected to the absorption bulb through a stout glass capillary tube (about 0·5 mm. bore) bent twice at right angles, with stout rubber junctions (Fig. 11). By opening the pinchcocks and raising the levelling tube, the gas is driven into the bulb, which is shaken for a few minutes. The gas is then drawn back into the burette and the diminution in volume noted. Since the volume is measured before and after absorption under the same conditions of pressure, temperature and moisture, no calculation is necessary, the diminution corresponding exactly to the volume of gas absorbed. The liquid used in the measuring apparatus consists, in the case of coal gas, of distilled water saturated with the same gas. The burette and bent tube are filled with this liquid by

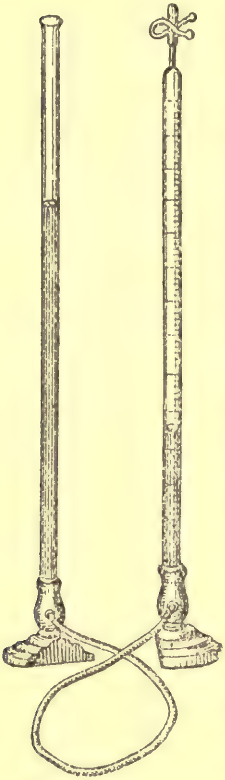


FIG. 10.

raising the reservoir, after which the inlet is closed. The burette is then put in communication with the gas-holder (taking care first to displace the air in the connecting tube), and about 100 c.c. of the sample are drawn in by gradually lowering the levelling vessel. The inlet is closed again and, after waiting about three minutes for the walls of the burette to drain, the liquid is adjusted to the same level in both limbs and the volume of gas read off.

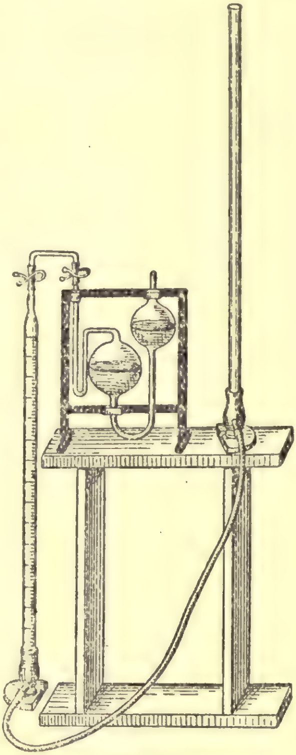


FIG. 11.

In transferring the gas to the absorption pipette, proceed in the following manner: First make sure that the pipette, which, like the measuring vessel, is provided with a short piece of rubber tube and a pinchcock, is filled to a definite mark, as near as possible to the lower edge of the rubber. Then connect the two vessels through the capillary tube and raise the levelling limb upon the stand, leaving both pinchcocks open until the whole of the gas has been driven into the pipette. Without disconnecting, rock the pipette to and fro, or allow the apparatus to rest for a few minutes, according to the directions given in each particular case (*vide infra*). Before retransferring the gas, pass about ½ c.c. of water into the bulb to prevent any of the absorbing solution which may have entered the capillary from being drawn back subsequently into the burette. Now lower the levelling vessel until the absorbent in the pipette again exactly reaches the mark, close the pinchcocks and disconnect the two vessels.

In order to obtain reliable results the following rules should be observed:

(1) The entire apparatus and all solutions employed should have acquired the temperature of the room before the experiment is started.

The temperature of the laboratory should be kept as uniform as possible throughout the analysis, and the apparatus should be shielded from gas flames and direct sunlight.

(2) The gas should always remain for three minutes in the burette before the volume is read.

(3) During this interval the gas should be under atmospheric pressure—*i.e.*, the liquid should be at the same level in both limbs of the apparatus, to minimize diffusion through the rubber tubing. For the same reason an unnecessarily high pressure (or suction) during the transference of the gas should be avoided.

(4) The thick-walled rubber tubing should be renewed frequently.

(5) Care should be taken that none of the absorbent is drawn into the burette.

In all cases the individual determinations must be performed in the precise order given below.

(*a*) **Determination of Carbon Dioxide.**—A gas pipette with two bulbs (Fig. 12) is employed; the absorbent is a concentrated solution of caustic potash (1 part KOH to 2 parts water).

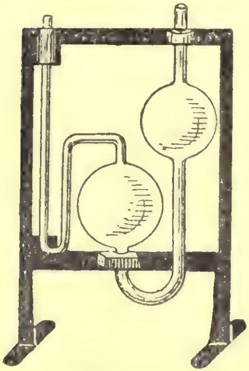


FIG. 12.

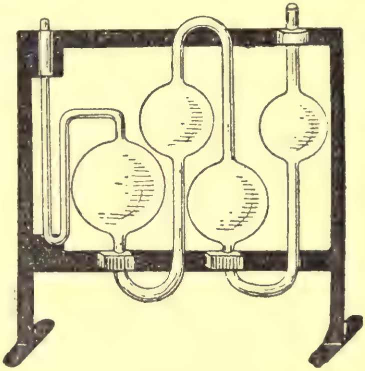


FIG. 13.

Reliable absorption value=40 c.c. CO_2 (see note below).

A brief agitation suffices for quantitative absorption. Before use the caustic potash in the pipette should be saturated with coal gas.

The term " absorption value " is used to denote the amount of gas which 1 c.c. of the absorbent can take up quickly and with certainty. Theoretically, a potash solution of the above concentration is capable of absorbing a much larger amount of carbon dioxide, but it is better to allow a considerable margin of safety than to risk using an almost exhausted absorbent. When a large number of analyses have to be performed, the analyst should keep a tabular record of the amount of gas absorbed by each pipette in successive experiments, so that he may know when a fresh solution is required.

(*b*) **Determination of " Heavy Hydrocarbons "**—*Absorbent: Saturated Bromine-Water containing a few Cubic Centimetres of Liquid Bromine.*—For this determination a four-bulb pipette (Fig. 13) is employed; the last two bulbs merely contain water, which is renewed whenever the unpleasant smell of bromine appears. The gas, after shaking for about five minutes with the bromine solution, is drawn back into the burette and immediately transferred to a pipette filled with caustic potash, which removes any bromine vapour. For this purpose it is advisable always to keep at hand a special pipette, which should be frequently refilled, since the hypobromite (KBrO) formed during the absorption, if present in any considerable amount, readily gives off oxygen.

The term " heavy hydrocarbons " refers to those compounds of carbon and hydrogen of relatively high density which are associated with methane in coal gas, such as benzene (C_6H_6), ethylene (C_2H_4), and acetylene (C_2H_2); they are difficult to separate and are often absorbed together (compare below).

The absorption of benzene by bromine-water is of a purely physical character, since, under the conditions of the foregoing experiment, the benzene is not brominated. Ethylene and acetylene form bromine addition products, the former $C_2H_4Br_2$, the latter $C_2H_2Br_2$ or $C_2H_2Br_4$. Of the heavy hydrocarbons contained in coal gas, benzene, although present in relatively small amounts, is the most important, owing to its exceptionally high heat of combustion, which greatly increases the calorific value of the gas. There are several, more or less troublesome, methods for the separate determination of benzene. That of St. Claire Deville consists in freezing it out of the coal gas. Harbeck and Lunge convert it into dinitrobenzene, in which form it is weighed. A simple and reliable volumetric method has been worked out by Denis and O'Neill, according to which the benzene is absorbed by shaking for three minutes with an ammoniacal solution of nickel. The reagent is prepared by dissolving 16 grs. of nickel nitrate in 180 c.c. of water, adding 2 c.c. of concentrated nitric acid, and stirring this solution into 100 c.c. of concentrated ammonia (sp. gr. 0·880). It is introduced into a two-bulb pipette and saturated with coal gas before use.

Benzene possesses the property of uniting with nickel salts in ammoniacal solution to form fairly stable nickel-ammonia-benzene compounds. Substances having the composition $Ni(CN)_2NH_3C_6H_6$ have already been isolated, and the nickel-ammonia-benzene compound formed in this case is probably similar.

When the calorific value of coal gas is calculated from analysis (see below), the separate determination of benzene is essential. The benzene is absorbed immediately after the determination of the carbon dioxide, and the rest of the hydrocarbons are then absorbed with bromine-water and recorded as ethylene.

(*c*) **Determination of Oxygen.**—There are several absorbents available for this purpose, of which, however, only one or two are suitable in all cases.

(1) *Alkaline Pyrogallol.*—A suspension of 10 grs. of pyrogallic acid in 30 c.c. of water is mixed with a solution of 240 grs. of caustic potash in 160 c.c. of water and used in a four-bulb pipette. Three minutes' shaking suffices for the absorption. The temperature of the solution employed should not be less than 15° C. Absorption value = 2 c.c.

This solution can be used in all cases. Its efficiency is due to the remarkable ease with which alkaline pyrogallol undergoes oxidation to carbon dioxide, acetic acid, and humic substances. The last named impart to the solution first a brown and then a black coloration.

(2) *Phosphorus.*—A pipette having the form shown in Fig. 14 is packed as closely as possible with sticks of white

phosphorus, and then filled completely with water. The pipette retains its efficiency for an unlimited period, but it should be protected from light, otherwise the phosphorus becomes converted into the red, inactive variety. The liquid in the measuring vessel must be renewed occasionally. The temperature of the absorbent should not fall below 20°. At this temperature absorption is complete in three minutes without shaking.

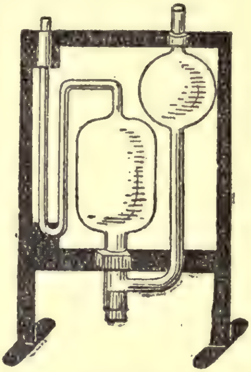


FIG. 14.

Traces of oxygen are present in all gases. The absorption of oxygen by phosphorus depends upon the oxidation of the latter to phosphoric or phosphorous oxides. Absorption does not take place, however, in the presence, even in small traces, of "heavy hydrocarbons," ammonia or alcohol. Similarly, if the amount of free oxygen in a gas exceeds 60 per cent., no oxygen is absorbed at ordinary pressure. Since a white cloud of phosphoric or phosphorous oxide always appears during the process of oxidation, it is easy to observe whether any reaction is taking place. Phosphorus glows when undergoing oxidation; hence, if the experiment is performed in a darkened room, a visible indication of the progress of the reaction may be obtained.

(3) *Copper Gauze.*—The pipette (Fig. 14) is packed with small rolls of bright copper gauze, over which is poured a mixture of equal volumes of a saturated solution of commercial ammonium carbonate and of 10 per cent. ammonia. Absorption value=6 c.c. The gas is kept in the pipette for five minutes without shaking. When the pipette is exhausted, only the solution need be renewed. This is a very convenient method of absorbing oxygen, but carbon monoxide and acetylene, if present, are also absorbed. The copper-ammonia pipette is generally employed in testing the oxygen used for mixing with hydrogen and methane in determination (*e*).

In this pipette part of the ammonia is oxidized to nitrite. The cupric oxide dissolves in the mixture of ammonium carbonate and ammonia, forming a blue cupric-ammonium salt,

$$CuO + (NH_4)_2CO_3 + 2NH_3 = Cu(NH_3)_4CO_3 + H_2O,$$

which on long standing is reduced by the excess of copper to a colourless cupro-ammonium salt,

$$Cu(NH_3)_4CO_3 + Cu = (CuNH_3)_2CO_3 + 2NH_3.$$

(*d*) **Determination of Carbon Monoxide**—(1) *Absorption Method.*—220 grs. of pure ammonium chloride are dissolved in 750 c.c. of water in a litre flask and mixed with 175 grs. of cuprous chloride. After shaking well, the solution is made up to the mark with 25 per cent. ammonia. One or more long spirals of copper wire should be placed in the stock-bottle, extending right up to the neck, in order to reduce any divalent copper compounds present in the solution. The reagent is used in a four-bulb pipette. Its absorption value is very small. To ensure accuracy, the bulk of the carbon monoxide should first be absorbed in a partly used pipette, and any residue finally absorbed in a second pipette filled with fresh cuprous chloride solution. At each absorption the pipette is shaken continuously for three minutes. Cuprous chloride also absorbs oxygen, acetylene and ethylene, which must therefore be previously removed.

The absorption of carbon monoxide by mixtures of cuprous chloride with ammonia or hydrochloric acid is due to the formation of a somewhat unstable compound, possibly Cu_2COCl_2, which decomposes on heating or under reduced pressure, liberating the carbon monoxide. Since, even at ordinary pressure, these solutions give up carbon monoxide on shaking, the precautions indicated above are necessary.

(2) *Combustion Method.*—See the determination of hydrogen and methane (*e*).

(*e*) **Determination of Hydrogen and Methane.**—These gases are determined together by exploding them with oxygen. A known volume of the residual gases from the preceding determinations is mixed with a measured volume of air or oxygen, and the mixture transferred to a stout pipette provided with sparking wires of platinum (Fig. 15).

This is connected with a levelling vessel containing mercury or water. The explosive mixture is fired by a spark from an induction coil. By measuring the contraction which takes place, as also the amount of carbon dioxide formed, or the volume of oxygen used in the combustion, the percentage of hydrogen and methane originally present in the sample may be calculated. Carbon monoxide can also be determined together with hydrogen and methane by the explosion method, instead of by absorption. In this case we are dealing with three unknown quantities; hence in every analysis three measurements are required—viz., the contraction in volume, the amount of carbon dioxide formed, and the amount of oxygen used. The following equations are required for the calculation:

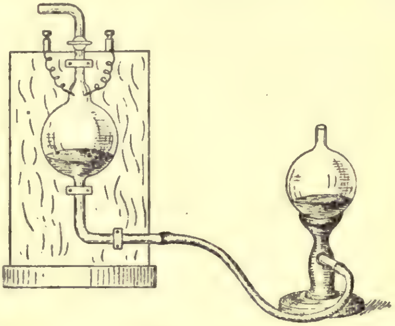


FIG. 15.

$$1.\ \underset{\text{(2 vols.)}}{2H_2} + \underset{\text{(1 vol.)}}{O_2} = \underset{\text{(0 vol.)}}{2H_2O} \text{ (liquid).}$$

$$2.\ \underset{\text{(1 vol.)}}{CH_4} + \underset{\text{(2 vols.)}}{2O_2} = \underset{\text{(1 vol)}}{CO_2} + 2H_2O.$$

$$3.\ \underset{\text{(2 vols.)}}{2CO} + \underset{\text{(1 vol.)}}{O_2} = \underset{\text{(2 vols.)}}{2CO_2}.$$

First Case: The carbon monoxide has been absorbed previously. The gas thus contains, besides the incombustible residue (nitrogen), only hydrogen and methane.

I. Calculation from the Contraction in Volume and the Amount of Carbon Dioxide produced.

In this case mercury should be used in the explosion pipette in preference to water, which would dissolve some of the carbon dioxide formed. After the explosion the gas is drawn back into the burette, where the contraction is measured; it is then transferred to a potash pipette and the amount of carbon dioxide determined. From equation (1) it follows that for every 2 vols. of hydrogen 3 vols. of gas disappear in the combustion. For x c.c. of hydrogen the contraction is therefore $\frac{3}{2}x$ c.c. In the combustion of 1 vol. of methane 2 vols. of gas, or for y c.c. of methane burnt $2y$ c.c. of gas, disappear.

The total contraction V_c is therefore

$$V_c = \tfrac{3}{2}x + 2y.$$

Now, y c.c. of methane furnish y c.c. CO_2; hence the volume of CO_2 found (V_{CO_2}) corresponds exactly to the volume of methane originally present. Substituting in the above equation y (methane) $= V_{(CO_2)}$, we get

$$x \text{ (hydrogen)} = \tfrac{2}{3}(V_c - 2V_{(CO_2)}).$$

Example: After absorbing the carbon dioxide, heavy hydrocarbons and carbon monoxide, 82·0 c.c. of residual gas remains. This is reduced to 12 to 15 c.c. by discharging a portion into the room, after which the volume measured is exactly 13·2 c.c. Air is now admitted, and a new reading taken.

Total volume = 99·6 c.c.

After the explosion the volume is 78·0 c.c.; hence the contraction $V_c = 21{\cdot}6$ c.c.

After treatment in the potash pipette the volume measures 73·2 c.c.; the amount of carbon dioxide is thus

$$V_{(CO_2)} = 78{\cdot}0 - 73{\cdot}2 = 4{\cdot}8 \text{ c.c.}$$

The 13·2 c.c. of residual gas therefore contain—

$$\begin{aligned}&\text{Methane} = 4{\cdot}8 \text{ c.c.}\\ &\text{Hydrogen} = \tfrac{2}{3}(21{\cdot}6 - 2 \times 4{\cdot}8) = 8{\cdot}0 \text{ c.c.}\end{aligned}$$

The remainder, $13{\cdot}2 - (4{\cdot}8 + 8{\cdot}0) = 0{\cdot}4$ c.c., is nitrogen.

If the residual gas were completely free from nitrogen, the contraction alone would suffice for the calculation of the two constituents; in this case the initial volume is $V = x + y$, and the contraction $V_c = \frac{3}{2}x + 2y$, from which we find

$$\begin{aligned}x &= 2(2V - V_c)\\ &= V - x.\end{aligned}$$

II. Calculation from the Contraction in Volume and Amount of Oxygen used.

In this case water may be used in the burette. As before, a portion of the residual gas is mixed with air or oxygen. If the latter be used, its purity should be previously determined in a copper gauze pipette. The gaseous mixture is fired and, without taking a reading, passed directly into a potash pipette, from which it is brought back to the burette, where the volume is measured. The excess of oxygen is ascertained by means of copper or phosphorus. The carbon dioxide having been absorbed, the contraction due to methane is now equal to three times its original volume ($=3y$), while that of hydrogen is the same as before; hence the total diminution in volume is

$$V_c = \tfrac{3}{2}x + 3y.$$

Now, 1 vol. of hydrogen requires $\frac{1}{2}$ vol. oxygen, and 1 vol. of methane 2 vols. oxygen; the total volume of oxygen, $V_{(O_2)}$, required is therefore

$$V_{(O_2)} = \tfrac{1}{2}x + 2y.$$

Solving both equations for x and y, we find

$$x = \tfrac{4}{3}V_c - 2V_{(O_2)},$$

and

$$y = V_{(O_2)} - \tfrac{1}{3}V_c.$$

Example : As before, 13·2 c.c. of residual gas are diluted with air to 99·6 c.c. The 84·4 c.c. of air added contain 18·0 c.c. oxygen. The volume of the gas after explosion and absorption of $CO_2 = 73{\cdot}2$ c.c.; hence

$$V_c = 99{\cdot}6 - 73{\cdot}2 = 26{\cdot}4 \text{ c.c.}$$

The excess of oxygen absorbed in the copper pipette amounts to 4·4 c.c.; hence the volume of oxygen used in the explosion is

$$V_{(2O)} = 18{\cdot}0 - 4{\cdot}4 = 13{\cdot}6 \text{ c.c.}$$

From this

$$x \text{ (hydrogen)} = \tfrac{4}{3} \times 26{\cdot}4 - (2 \times 13{\cdot}6) = 8{\cdot}0 \text{ c.c.}$$
$$y \text{ (methane)} = 13{\cdot}6 - (\tfrac{1}{3} \times 26{\cdot}4) = 4{\cdot}8 \text{ c.c.}$$

Second Case: The gas still contains carbon monoxide, hydrogen, and methane. A measured volume of oxygen is added and the mixture exploded over mercury, as before. After measuring the contraction, the carbon dioxide is determined and then the excess of oxygen. The contraction due to hydrogen is the same as in I. From equation 3 (see p. 51) it is found that in the explosion of 2 vols. of carbon monoxide 1 vol. of oxygen disappears, or $\frac{1}{2}z$ c.c. of oxygen for z c.c. of carbon monoxide. The total contraction is thus

$$V_c = \tfrac{2}{3}x + 2y + \tfrac{1}{2}z.$$

Since 1 vol. of carbon monoxide yields, like methane, 1 vol. of carbon dioxide, the total volume of carbon dioxide formed will be

$$V_{(CO_2)} = y + z.$$

Finally, in calculating the consumption of oxygen, since 2 vols. of carbon monoxide require for combustion 1 vol. of oxygen, we have still to add $\frac{1}{2}z$ c.c.

The total volume of oxygen used is therefore

$$V_{(O_2)} = \tfrac{1}{2}x + 2y + \tfrac{1}{2}z.$$

Solving the three equations for x, y, and z, we find

$$x \text{ (hydrogen)} = V_c - V_{(O_2)},$$
$$y \text{ (methane)} = V_{(O_2)} - \tfrac{1}{3}(V_c + V_{(CO_2)}),$$
$$z \text{ (carbon monoxide)} = \tfrac{1}{3}(4V_{(CO_2)} + V_c) - V_{(O_2)}.$$

The gaseous mixture, instead of being exploded, may be slowly burned in the pipette shown in Fig. 16. A quantity of the gas is introduced into the pipette. The thin platinum wire stretched between the brass terminals is then heated to redness by passing an electric current and an ample (measured) quantity of oxygen, previously tested for purity, is passed in slowly from a burette, so that the combustion proceeds quietly without explosion. The advantage of this method is that

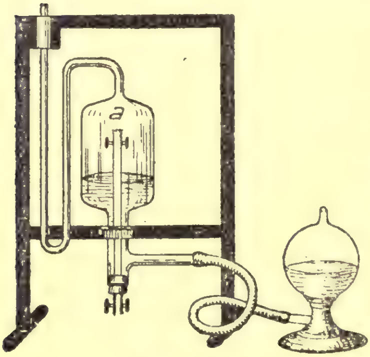


FIG. 16.

larger volumes of gas (if necessary, the whole of the residue from the preceding determination) can be burned.

The methods and apparatus used for the analysis of coal gas are also applicable to the technical investigation of all other heating and illuminating gases, such as flue gas, producer gas, water gas, and Dowson gas. Gases which contain so little combustible matter that they fail to explode with air or oxygen are mixed with either a measured volume of hydrogen or a suitable quantity of electrolytic gas before ignition. In the latter case the volume need not be measured, since it disappears completely in the explosion.

2. Determination of Total Sulphur.

The method consists in burning a large volume of coal gas with air and absorbing the oxides of sulphur produced. A large inverted flask (Fig. 17) serves as combustion chamber, the wide neck being constricted at the bottom to connect with a delivery tube. The coal gas, after passing through a small experimental meter, is led into the globe through

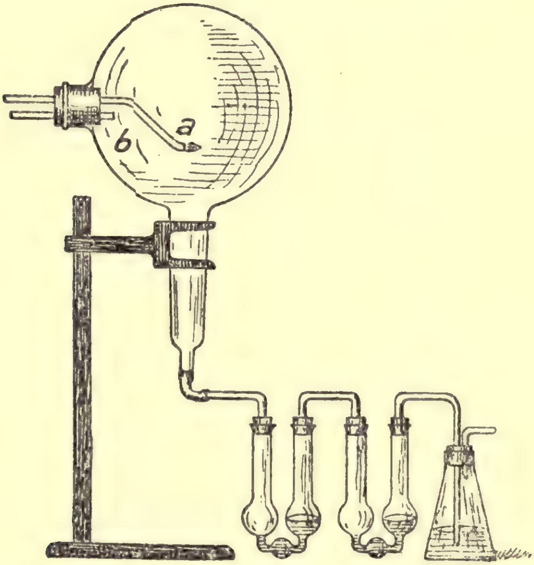
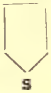
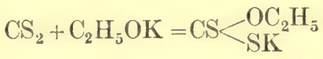


FIG. 17.

the tube *a*, which terminates in a jet, while the air, previously washed with concentrated caustic potash solution, enters through *b*. The outlet is connected by a piece of thick rubber tubing with a series of two or three wash-bottles containing about 100 c.c. of commercial hydrogen peroxide previously neutralized by careful titration with 1/5 normal caustic soda, using methyl orange as indicator. In starting the experiment, the cork is removed from the flask, the gas is turned on, and, after making sure that all the air has been displaced from the meter, is ignited at the jet, the supply being regulated by means of a screw clip to produce a flame about 1 c.cm. long. The stopper is now replaced, and a strong current of air drawn through the apparatus by means of a suction pump. About 50 litres of gas should be burned, the experiment lasting approximately three and a half hours. The whole of the sulphur originally present in the gas is now contained in the hydrogen peroxide as sulphuric acid, which may be titrated directly with 1/5 normal caustic soda solution.

Of the sulphur compounds present in the unpurified gas, by far the greater proportion consists of hydrogen sulphide. In addition to this, the gas invariably contains a small quantity of carbon disulphide (CS_2), together with traces of carbon oxysulphide (COS), thiocyanic acid ($HCNS$), mercaptan (C_2H_5SH) and thiophene ; the purified gas should not contain more than a slight trace of hydrogen sulphide. Purification is generally effected by means of iron oxide (see p. 70), but this does not remove carbon disulphide, which is consequently the chief sulphur compound remaining in the purified gas used for street lighting. Carbon disulphide may be detected by the following qualitative test (Vogel's method): Coal gas, after drying over calcium chloride, is passed through a bottle containing a solution of caustic potash in absolute alcohol. If carbon disulphide be present, potassium xanthate is formed, according to the equation



$$CS_2 + C_2H_5OK = CS{<}^{OC_2H_5}_{SK}$$

The alcohol is then evaporated and the residue slightly acidified with acetic acid. On adding a few drops of copper sulphate solution a brown precipitate of cupric xanthate is produced, which quickly changes to yellow cuprous xanthate.

Sulphur, in whatever form it may exist, is highly objectionable in gas used for illuminating purposes, owing to the detrimental effects of its combustion products upon metal objects and paint, apart from considerations of health.

Of the other impurities in gas used for public lighting, naphthalene, ammonia, and cyanogen are sometimes determined quantitatively. Naphthalene, on account of its high vapour pressure, is conveyed long distances in the pipes, and tends to separate out and block the mains, especially in cold weather. Not more than the merest trace of ammonia and cyanogen compounds should be present in the purified gas, since these on combustion may produce oxides of nitrogen.

3. Calculation of the Calorific Value.

The calorific value of coal gas, like that of gaseous fuels in general, may be obtained approximately by adding together the heats of combustion of its constituents. The following molecular heats of combustion are required:

*Hydrogen ..	68·4 Cals.
*Methane ..	212·0 ,,
Carbon monoxide	68·0 ,,
*Benzene ..	790·0 ,,
*Ethylene ..	333·4 ,,

*Assuming the water formed in the combustion to be *condensed.*

Suppose that a gas, on analysis, is found to have the following composition:

	Percentage by Volume.
Hydrogen	49·2
Methane	34·0
Carbon monoxide	7·8
Benzene	1·9
Ethylene	3·1
Carbon dioxide	1·6
Nitrogen	2·4

The calorific value of 1 cb.m. of the gas at 15° C. and 760 mm. works out at 5,772 Cals. This is the *maximum* value.

If, however, the water produced remains in the form of steam, the heat of combustion of hydrogen is only 57·6 Cals., while the heats of combustion of the gases containing this element are correspondingly lowered at the rate of 10·8 Cals. for every molecule of water produced. The value obtained by substituting these lower heats of combustion is the *net* calorific value (=5,182 Cals.). The student should make these calculations for himself from the results of his own analysis.

The determination of calorific value is regularly performed in gasworks practice, usually by means of the convenient Junker calorimeter. Other routine determinations are those of the illuminating power and specific gravity of the purified gas. The illuminating power—*i.e.*, the intensity of the light emitted by the gas burning freely in air—depends upon the amount of heavy hydrocarbons present; these decompose in burning, with the separation of minute particles of carbon, which become incandescent at the very high temperature of the flame. If, however, an excess of air be mixed with the gas during combustion (as in the Bunsen burner), a non-luminous flame is produced, owing to the fact that the carbon, instead of separating in the elemental condition, is immediately oxidized. Under the old system of burning coal gas in ordinary jets, the estimation of illuminating power was very important; but it has lost much of its significance since the introduction of incandescent lighting, in which the gas itself burns with a non-luminous flame, *heating* to incandescence a mantle of rare earths (99 per cent. thoria and 1 per cent. ceria). On the other hand, the determination of the specific gravity has become more important, owing to the modern practice of admixing water gas with coal gas. The density of coal gas can be calculated from its composition, but in practice it is usually determined experimentally by means of Schilling's apparatus (p. 61).

Coal gas is manufactured by heating coal in absence of air (dry distillation). The coal is charged into cylindrical retorts made of fireclay, which are placed either horizontally or, of late years, vertically or obliquely. These are heated in a recuperative furnace with producer gas or Dowson gas to about 1,200° to 1,400° C. During the first stage of the distillation the tar and a large amount of heavy hydrocarbons escape, but as the temperature rises the hydrocarbons undergo increasing decomposition, with the separation of hard retort carbon, which remains behind as a valuable by-product.

From the retorts the gas passes up a tube into the hydraulic main (Fig. 18), where a portion of the tar separates out. The hydraulic main serves as a seal to shut off direct connection between the retorts and the gas main, thus preventing access of air to the latter when the retorts are opened for discharging. The crude gas is then cooled, to cause a further deposition of the tar. This is effected by passing it through an iron cylinder containing an arrangement of tubes kept cool by a stream of water flowing counter to the incoming gas. The gas then enters the washer or scrubber, where it comes into contact with jets of water which absorb the ammonia, most of the carbon dioxide, and part of the hydrogen sulphide and hydrocyanic acid. To remove the last traces of tar, the gas is led into a separator consisting of three parallel plates with numerous slot perforations, arranged in such a way that the gas passing through a hole in one plate impinges upon the wall of the next, where the tar collects (Fig. 19). Finally the gas is freed from any remaining hydrogen sulphide and hydrocyanic acid by passing it over hydrated iron oxide (see p. 70), and is then stored in the gas-holder.

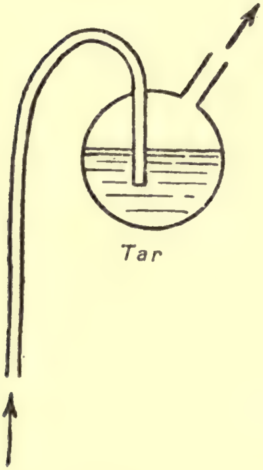


Fig. 18.

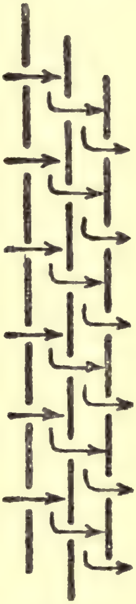


Fig. 19.

Coal gas, after purification, has approximately the following composition:

	Percentage by Volume.
Hydrogen	45 to 50
Methane	30 to 35
Carbon monoxide	8 to 10
Heavy hydrocarbons	3 to 5
Carbon dioxide	1 to 2
Nitrogen	2 to 4

4. BALLOON GAS.

1. Volumetric Analysis.—The analysis is performed exactly as described under Coal Gas. The specific gravity of the gas can be calculated from the analysis, but is generally ascertained by experiment.

2. Specific Gravity.—The apparatus devised by Schilling for the determination of the specific gravity of coal gas is employed (Fig. 20). *A* is a glass vessel about 40 cm. in height. Resting upon its upper rim is a metal cap, *C*, which supports the glass cylinder *B*. The latter extends almost to the base of the outer vessel; it is open at the bottom and is constricted near both ends. Passing through the plate are two tubes, one of which, *d*, is provided with an ordinary stopcock and nozzle, the other, *e*, with a two-way tap which enables connection to be established either through a nozzle or with the opening *f*. This opening is covered by a thin platinum disc pierced with a very fine hole. The thermometer *t* is graduated in fifths of degrees. The apparatus is filled to a mark near the top of the vessel *A* with distilled water or tap-water from which any carbon dioxide has been displaced by saturation with air.

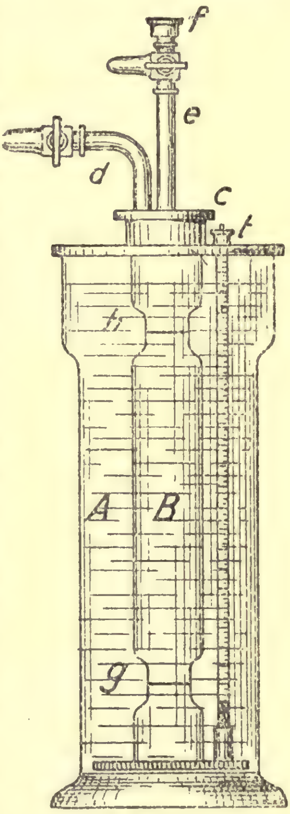


FIG. 20.

Air is admitted to the cylinder *B* by gradually raising this with the cock *d* open, after which *d* is closed and the air expelled through the nozzle at *e*. This operation is repeated several times. Finally, the cylinder is filled almost completely with air. After waiting for three minutes to allow the water to drain from the wall of the vessel, the two-way tap *e* is turned quickly to communicate with *f*. As the air escapes through the fine orifice at *f*, and the cylinder sinks, the time which elapses between the coincidence of the water level with the lower and upper marks, *g* and *h* respectively, is recorded by means of a stop-watch reading to one-tenth of a second. The experiment is repeated several times, and the readings should agree to within one-fifth of a second. A number of determinations are made in the same way with the sample of gas to be tested, after the water in the container has been saturated with the particular gas. The temperature of the water should remain unchanged throughout the experiment.

According to Graham and Bunsen's law, the time taken by different gases to diffuse through a small orifice is proportional to the square of their densities; hence, if air requires t seconds and the gas t_1 seconds, to pass from the cylinder, the specific gravity of the gas s (taking the density of air=1) is

$$s=\frac{t_1^2}{t^2}.$$

Under the conditions of the above experiment the gases are saturated with water vapour, which, of course, affects their density, rendering a correction necessary when s is calculated for the dry gas.*

If $S_{(air)}$ represent the density of dry air at 0° C. and 760 mm.,

$S_{(gas)}$ the density of the gas under investigation, dry at 0° C. and 760 mm.,

$S_{(H_2O)}$ the density of water vapour at 0° C. and 760 mm.,

---

* It is remarkable that in previous descriptions of Schilling's method this correction is either not mentioned at all, or is regarded as unnecessary, because the gas and air are both saturated with moisture. That this view is erroneous follows from the formula deduced below.

e the tension of water vapour at the temperature of the experiment,

and

p the pressure of the gas during the experiment,

then the density of air saturated with water vapour at the absolute temperature T is

$$=\left[S_{(\text{air})}\frac{p-e}{760}+S_{(H_2O)}\frac{e}{760}\right]\frac{273}{T},$$

and the density of the moist gas under investigation is

$$=\left[S_{(\text{gas})}\frac{p-e}{760}+S_{(H_2O)}\frac{e}{760}\right]\frac{273}{T}.$$

The value s found in the experiment represents the ratio of these densities—*i.e.*,

$$s=\frac{S_{(\text{gas})}\,(p-e)+S_{(H_2O)}\,.\,e}{S_{(\text{air})}\,(p-e)+S_{(H_2O)}\,.\,e}.$$

Taking the density of air, $S_{(\text{air})}=1$, that of water vapour $S_{(H_2O)}$ is $=0{\cdot}6215$; hence

$$S_{(\text{gas})}=\frac{[(p-e)+0{\cdot}6215\times e]s-0{\cdot}6215\times e}{p-e}.$$

In this formula, p is taken as the average pressure of the gas during the experiment.

If the pressure read on the barometer is b mm. of mercury, and the gas stands under an excess pressure of a cm. of water when the cylinder is immersed to the lower mark g, and an excess pressure of c cm. of water at the upper mark h, the mean excess pressure is $=\frac{a+c}{2\times1{\cdot}36}$ mm. mercury (sp. gr. 13·6), and the total pressure $p=b+\frac{a+c}{2\times1{\cdot}36}$.

Example : In the above experiment air required on an average 245·4 seconds to diffuse through the orifice, the gas 71·3 seconds. The ratio of the specific gravities of the moist gases is therefore

$$s=\frac{71{\cdot}3^2}{245{\cdot}4^2}=0{\cdot}0844.$$

The experiment was conducted at 20° C., at which temperature the tension of water vapour $(e) = 17{\cdot}4$ mm. mercury.

The barometric pressure was 759 mm., the maximum excess pressure in the cylinder = 31 cm. water, the minimum excess pressure = 7·1 cm. water; hence $p = 759 + \frac{31 + 7{\cdot}1}{2 \times 1{\cdot}36} = 773$ and $(p - e) = 773 - 14{\cdot}7 = 755{\cdot}6$. The specific gravity of the dry gas relative to that of air, taken as unity, is therefore

$$S_{(\text{gas})} = \frac{(755{\cdot}6 + 10{\cdot}66)0{\cdot}0844 - 10{\cdot}66}{755{\cdot}6} = 0{\cdot}0715.$$

The suitability of a gas for use in air-ships is judged solely by its specific gravity, since it is upon this that the buoyancy depends. The impurities present are of no consequence provided they are not of such a nature as to injure the fabric of the balloon, like corrosive vapours liable to be introduced with hydrogen prepared by the decomposition of acids. The buoyancy of an enclosed gas in a heavier gas is given by the difference of their densities.

A litre of air at 0° and 760 mm. weighs 1·293 grams, a litre of hydrogen under the same conditions 0·09 gram. The buoyancy of hydrogen in air under normal conditions is thus

$$1{\cdot}293 - 0{\cdot}09 = 1{\cdot}203 \text{ litre-grams, or cubic-metre-kilograms.}$$

Since the density of a gas increases proportionally with the pressure and decreases proportionally with the absolute temperature, the same must also apply to the buoyancy; hence the buoyancy of pure hydrogen in air is given by the general expression

$$1{\cdot}203 \times \frac{b}{760} \times \frac{273}{T}.$$

For instance, at 20° C. and 740 mm. pressure it is = 1·091 cb.m.-kg. To calculate the buoyancy of a gas from its density (S) determined in the above experiment, compared with air = 1, the following equation is used:

$$\text{Buoyancy (at } 0° \text{ and } 760 \text{ mm.)} = (1 - S) \times 1{\cdot}293 \text{ cb.m.-kgr.};$$

or, in general,

$$= (1 - S) \times 1{\cdot}293 \times \frac{b}{760} \times \frac{273}{T}.$$

The buoyancy of the gas under examination may be simply and conveniently expressed as a percentage of the theoretical buoyancy. Thus the density of pure hydrogen, referred to air =1, is 0·0696; and its buoyancy calculated from the specific gravity and expressed as above is

$$x = \frac{(1 - S) \times 100}{1 - 0·0696} = \frac{(1 - S) \times 100}{0·9304} \text{ per cent.}$$

The numerical value so obtained corresponds to the percentage of hydrogen contained in a sample of this gas, in which the impurities either have the same density as air or are calculated in terms of air.

Thus, substituting in the above equation the value 0·0715 (the specific gravity of the dry gas), we get

$$\frac{1 - 0·0715 \times 100}{0·9304} = 99·8 \text{ per cent.—}$$

i.e., the buoyancy of this gas is 99·8 per cent. of that theoretically possible, and is also equal to that of a gas containing 99·8 per cent. hydrogen with 0·2 per cent. air, or, so far as concerns its use in air-ships, hydrogen with 0·4 per cent. of a gas having only one-half the density of air, or 0·1 per cent. of a gas twice as heavy as air.

Similarly, coal gas having a specific gravity of 0·431, used in a balloon, would correspond to a gas containing

$$\frac{1 - 0·431 \times 100}{0·9304} = 61·2 \text{ per cent.}$$

of hydrogen.

Coal gas is still extensively employed for filling ordinary balloons. Dirigible air-ships, which on account of their motors and fittings carry a much heavier load, require the purest hydrogen obtainable (98 to 99 per cent.). The commercial production of large quantities of hydrogen of this degree of purity at a low cost is a problem which is being strenuously investigated at the present time. A large amount of very pure hydrogen is obtained as a by-product in the electrolytic chlorine process, but the transport of the gas in steel cylinders adds greatly to its price. What is wanted is a simple and inexpensive method of generating hydrogen on the spot. Many processes have been suggested, and it remains to be seen which of these is best adapted to industrial requirements.

5. SPENT OXIDE.

1. Determination of Moisture.—About 30 grs. of the sample are powdered as finely as possible and dried at ordinary temperature until constant in weight. The air-dried substance is used in determinations (2) and (3).

Some analysts prefer to dry the sample at 50° to 60° C., but at this temperature cyanogen may be lost.

2. Determination of Sulphur.—The method consists in extracting the sulphur with carbon disulphide; 100 c.c. of the freshly distilled solvent are poured into a 200 c.c. round-bottomed flask which is connected through a sound *bark* cork with a Soxhlet extraction apparatus having an efficient reflux condenser; 15 grs. of the pulverized air-dried sample are placed in the filter-cone within the extractor. Before starting the distillation, it is advisable to moisten the substance with carbon disulphide and to plug the mouth of the filter with a loose wad of cotton-wool, otherwise the powder is apt to be dispersed by the drops of liquid falling from the condenser. After about twenty extractions the whole of the sulphur should be in solution. The solution may also contain tar substances derived from the crude gas; these are removed by adding a little potassium carbonate, together with 1 gr. of animal charcoal, and allowing the mixture to stand overnight. Next day it is filtered into a weighed flask. The carbon disulphide is evaporated by immersing the flask in warm water and the residual sulphur weighed.

As mixtures of carbon disulphide and air readily explode, the final operation should be done in a draught chamber in which no flame is burning, either beneath the water-bath or in the flue.

3. Determination of Cyanogen: Feld's Method.—Triturate 0·5 gr. to 2 grs. of the air-dried sample in a glazed porcelain dish for about five minutes with 1 c.c. of a normal solution of ferrous sulphate and 5 c.c. of 30 per cent. sodium hydroxide. Then add 10 c.c. of a 3 N solution of magnesium chloride, and wash the whole with hot water into a 750 c.c. Erlenmeyer flask of resistance glass. Add a further 20 c.c. of the magnesium chloride solution and dilute with water to 150-200 c.c. Boil for five minutes, add 100 c.c. of a hot solution of decinormal mercuric chloride and heat again for five to ten minutes.

The contents of the flask have now to be distilled with sulphuric acid. For this purpose the flask is provided with a well-fitting rubber stopper, through which pass (1) a long glass tube dipping into the solution, to serve for the admission of air; (2) the stem of a dropping funnel; (3) a short bent tube connected with a sloping condenser, which delivers the distillate into a wash-bottle containing 20 c.c. of 8 per cent. caustic soda solution.

Without allowing the contents of the flask to cool, 30 c.c. of 4 N sulphuric acid are run in from the dropping funnel and the mixture is distilled for twenty minutes. During the distillation a slow current of air is drawn through the apparatus by means of a water-pump. The alkaline solution of hydrocyanic acid in the receiver is then determined by Liebig's method of direct titration with decinormal silver nitrate solution, using potassium iodide as indicator.

The most important of the cyanogen compounds present in spent oxide is Prussian blue, $Fe_4[Fe(CN)_6]_3$; there are also varying amounts of thiocyanates, ammonium cyanide, ferrous ammonium cyanide, and certain obscure compounds. The determination of total cyanogen is of little consequence, since only that portion which can be profitably extracted in the form of ferrocyanide is of commercial value. The less valuable thiocyanates are determined independently (see under 5).

The following reactions occur in the analysis: By treatment with caustic soda and ferrous sulphate, the Prussian blue and any simple cyanides present are converted into soluble sodium ferrocyanide,

$$Fe_4[Fe(CN)_6]_3 + 12NaOH = 3Na_4Fe(CN)_6 + 4Fe(OH)_3,$$

and

$$6NaCN + {}^{*}Fe(OH)_2 = Na_4Fe(CN)_6 + 2NaOH.$$

---

* From the interaction of ferrous sulphate and caustic soda.

Magnesium chloride is added to remove the excess of alkali,

$$MgCl_2 + 2NaOH = Mg(OH)_2 + 2NaCl,$$

which otherwise, on boiling, would dissolve some of the sulphur, with the possible formation of thiocyanates.

The original cyanogen compounds, now present as sodium ferrocyanide, are converted, by boiling with mercuric chloride, into mercuric cyanide:

$$Na_4Fe(CN)_6 + 3HgCl_2 + Mg(OH)_2 \\ = 3Hg(CN)_2 + 4NaCl + Fe(OH)_2 + MgCl_2.$$

Finally, by the addition of dilute sulphuric acid, hydrocyanic acid is liberated and distilled into caustic soda, by which it is absorbed. In titrating the alkaline solution of hydrocyanic acid by Liebig's method, according to the equation

$$2NaCN + AgNO_3 = NaAgCN_2 + NaNO_3,$$

note that 108 grs. of Ag are equivalent to 52 grs. of $(CN)_2$.

4. Determination of Ammonia—(*a*) *Ammonia Soluble in Water.*—25 grs. of the original undried substance are covered with cold water in a 500 c.c. flask and shaken at intervals over a period of twenty-four hours.

After adding a few cubic centimetres of magnesium chloride to assist the filtration, the flask is filled to 512 c.c. (12 c.c. allowed for the volume of the solid) and the solution passed through a *dry* filter; 200 c.c. of the filtrate are transferred to a flask (Fig. 26) and distilled with caustic soda. The ammonia liberated is absorbed in excess of normal sulphuric acid, which is titrated back with caustic soda solution.

(*b*) *Total Ammonia.*—10 grs. of the undried substance are distilled directly with caustic soda.

$(b-a)$ gives the amount of " ammonia insoluble in water."

The water-soluble ammonium compounds present in the spent oxide are chiefly the cyanide, NH_4CN, thiocyanate, NH_4CNS, and ferrocyanide, $(NH_4)_4Fe(CN)_6$; the insoluble compounds are salts of ferrocyanic acid in which the base is partly iron and partly ammonium—*e.g.*, the ferrous ammonium ferrocyanides having the formula $(NH_4)_2''FeFe(CN)_6$ and $(NH_4)_6''Fe[Fe(CN)_6]_2$.

5. Determination of Thiocyanates.—Only the soluble ammonium thiocyanate is determined.

(*a*) *By the Colorimetric Method* (*Pfeiffer's Method*).—20 c.c.

of the extract prepared for the determination of "water-soluble" ammonia (equal to 1 gr. of the original sample) are diluted with 80 c.c. of water and mixed in a beaker with 1 c.c. of hydrochloric acid and 1 c.c. of a 5 per cent. solution of ferric chloride. A standard solution consisting of 100 c.c. of water, 1 c.c. of hydrochloric acid, and 1 c.c. of 5 per cent. ferric chloride solution, is titrated in a similar vessel with a centinormal solution of ammonium thiocyanate until the tint corresponds to that of the test solution made up to the same volume with distilled water from a burette; the comparison should be made with the beakers placed close together on a sheet of white paper.

This method gives a sufficiently accurate result when the spent oxide, as is usually the case, contains only a small quantity of thiocyanate. If larger amounts are present, the following method should be employed:

(*b*) *By the Gravimetric Method.*—100 c.c. of the extract prepared for the determination of ammonia are heated and mixed with excess of barium chloride to precipitate any sulphates present, which are filtered off. The filtrate is again heated to boiling, acidified strongly with nitric acid and kept on the boil for a few minutes; the fresh precipitate of barium sulphate is filtered off and weighed in the usual way.

The sulphur in thiocyanates is readily oxidized to sulphuric acid,

$$2HCNS + 3O_2 + 2H_2O = 2HCN + 2H_2SO_4.$$

Chlorine or bromine may be used in place of nitric acid. Potassium permanganate brings about a quantitative oxidation even in the cold. This operation should be conducted in a draught chamber, on account of the hydrocyanic acid liberated.

The above methods are also used in the analysis of cyanide mud or cyanide cake obtained from Bueb's wet purification process. In this case cyanogen, thiocyanate, and total ammonia are determined.

Determination of Cyanogen.—25 grs. of the well-mixed cyanide slime, or 10 grs. of cake, are boiled for three-quarters of an hour with 50 c.c. of a 20 per cent. solution of caustic soda and 200 c.c. of distilled water to expel the ammonia.

After cooling, the mixture is transferred to a 500 c.c. flask, diluted to 505 c.c. with water (5 c.c. from a pipette), and passed through a dry filter; 10 to 15 c.c. of the filtrate are then treated as described under (3).

Determination of Ammonia.—5 grs. of the cyanide slime or cake are distilled with excess of caustic soda as described under 4 (*b*).

Determination of Thiocyanate.—5 grs. of the cyanide slime or cake are digested with water in a 500 c.c. flask for one to two hours, with frequent shaking. The extract is diluted to the mark and passed through a dry filter; 100 c.c. of the filtrate are treated as in 5 (*b*).

In the old method of purification the crude coal gas was passed through chambers containing slaked lime, which retains the carbon dioxide and other impurities. Calcium hydroxide combines with hydrogen sulphide to form calcium hydrosulphide, $Ca(SH)_2$, and with hydrocyanic acid to form calcium cyanide or thiocyanate. Any carbon disulphide present reacts with the hydrosulphide, forming calcium thiocarbonate,

$$Ca(SH)_2 + CS_2 = CaCS_3 + H_2S.$$

Subsequently, hydrated iron oxide came into use as a purifying agent, first in the form of Laming's compound, which consisted of a mixture of ferrous sulphate with excess of lime, and later on without the addition of lime.

Natural iron hydroxide, which occurs as bog-ore, is most suitable for the purpose, but the caustic lye residues from the extraction of bauxite are also used (Lux's mass).

In contrast to lime, ferric hydroxide possesses the advantage of being easily regenerated. With hydrogen sulphide it forms ferric sulphide,

$$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O,$$

which in the *moist* state, in contact with air, readily gives up free sulphur,

$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S.$$

The purifier is regenerated over and over again until its sulphur content has risen to 40 to 60 per cent.

As already stated, the hydrocyanic acid is absorbed as Prussian blue, $4Fe(CN)_3.3Fe(CN)_2$, which remains unchanged during the regeneration process, and gradually accumulates to about 15 per cent. If the gas contains ammonia, some ammonium thiocyanate is also formed. Frequently, the crude gas is mixed with 1 to 2 per cent. of air, which immediately reconverts the ferric sulphide in the mass into oxide. The ferric hydroxide may thus be regarded as a catalyst in the reaction

$$2H_2S + O_2 = 2S + 2H_2O.$$

The purification process takes place in a series of iron chambers in which the crushed bog-ore is spread on trays placed one above another.

Spent oxide has become one of the most important raw materials for the manufacture of cyanides. It is usually treated as follows: After extracting with water to recover the soluble ammonium salts, lime is added to convert the Prussian blue into soluble calcium ferrocyanide, $Ca_2Fe(CN)_6$. The solution is then filtered, concentrated, and treated with potassium chloride, whereupon a precipitate of potassium calcium ferrocyanide, $K_2CaFe(CN)_6$, separates out in a very pure form. This salt is dissolved in water, and the calcium replaced by the addition of a calculated quantity of potash. A solution of pure potassium ferrocyanide is thus obtained, which is evaporated *in vacuo* to the point of crystallization.

The residue, free from cyanide, goes to the sulphuric acid plant, where the sulphur is utilized.

The method of purification just described, although very convenient, has several disadvantages. Sometimes the cyanogen is incompletely removed from the crude gas, a considerable amount remaining in the domestic supply; this is not only deleterious to health, but also uneconomical, considering the high price of cyanogen compounds. Secondly, the extraction of the relatively small amount of cyanogen compounds from the spent oxide is rendered difficult by the large quantity of sulphur present.

Other methods of purification, by which the hydrogen sulphide and cyanogen can be absorbed separately, are coming into favour. Bueb's process appears to give the most favourable results. In this the crude gas, freed only from tar and naphthalene, and still containing all the ammonia, is passed through a solution of ferrous sulphate. The whole of the cyanogen is absorbed with the formation of insoluble ferrous ammonium ferrocyanide, $(NH_4)_6Fe[Fe(CN)_6]_2$, while the liberated $-SO_4$ ion from the ferrous sulphate immediately combines with ammonia, forming ammonium sulphate. The gas is then freed from the remaining ammonia by washing with water, as described above, and finally passed over hydrated iron oxide, which, owing to the absence of cyanogen, can now be more fully utilized. The cyanide slime from the wash-towers is then separated from the ammonium sulphate solution in a filter-press, and the cake so obtained, which contains about 30 per cent. cyanogen, is used for the production of potassium ferrocyanide by a method similar to that employed in the older process for the dry treatment of the spent oxide. The spent oxide, now free from cyanogen compounds, goes to the sulphuric acid works.

6. PYRITES.

1. Determination of Sulphur (Lunge's Method).—0·5 gr. of the very finely ground and carefully sifted sample is heated gently with 10 c.c. of aqua regia (prepared by mixing 3 parts of nitric acid, sp. gr. 1·4, with 1 part of concentrated hydrochloric acid, sp. gr. 1·19) in a beaker covered with a watch-glass. Should any sulphur separate out, a few grains of potassium chlorate are cautiously introduced.

After heating for a few minutes, add 5 c.c. of concentrated hydrochloric acid and evaporate to dryness. Moisten the residue with 1 c.c. of concentrated hydrochloric acid and take up with 100 c.c. of hot distilled water. Without filtering, make just alkaline with ammonia, then add a further 5 c.c. of 25 per cent. ammonia. Heat for about a quarter of an hour at 70° C., filter, wash the precipitate with hot water until a few drops of the washings, boiled with barium chloride solution, show no turbidity even after standing for some minutes; add the washings to the filtrate and, if necessary, reduce the volume to 400 to 450 c.c. by evaporation.

Neutralize with dilute hydrochloric acid; then add 1 c.c. of concentrated hydrochloric acid, heat to boiling, run in *very gradually* 20 c.c. of a hot solution of 10 per cent. barium chloride drop by drop with constant stirring and set the beaker on a water-bath for thirty minutes.

Filter off the precipitate of barium sulphate, burn moist in a platinum crucible, ignite with the crucible on the slant and weigh.

Pyrites, FeS_2, is the most important source of sulphur for the manufacture of sulphurous and sulphuric acids. It is frequently associated with copper pyrites, FeS(CuS), and occasionally also with zinc blende, ZnS, and galena (PbS). All these sulphides, on treatment with aqua regia, are oxidized to sulphates. On extraction with water, the insoluble lead sulphate, and also any barium sulphate originally present, remain with the gangue.

The sulphur combined with lead and barium is not set free in the ordinary process of roasting, since the temperature employed is insufficient to decompose these compounds. Hence, the percentage of sulphur found by Lunge's method corresponds exactly to that available in practice.

The evaporation with hydrochloric acid is intended to expel the last traces of nitric acid, since barium nitrate is readily occluded by barium sulphate.

Even more important is the removal of iron. Barium sulphate precipitated from solutions containing ferric salts is invariably found to be contaminated with iron, probably owing to the formation of a barium-iron complex. In precipitating the iron with ammonia, follow the directions carefully. By using the prescribed amount of ammonia and heating at 70° C. the formation of basic ferric sulphate is prevented, but a large excess of ammonia should be avoided, as the barium sulphate precipitate is liable to bring down ammonium salts formed during the subsequent neutralization.

The ignition of the moist barium sulphate on the filter saves time, but necessitates a second heating in the open, inclined crucible to oxidize any sulphate previously reduced to sulphide. For this purpose a good burner is preferable to the blowpipe.

2. Determination of Copper.—5 grs. of the sample are weighed into an Erlenmeyer flask, and 60 c.c. of 30 per cent. nitric acid added gradually through a funnel. When the vigorous reaction has subsided, the solution is heated on a sand-bath until fumes of sulphuric acid appear. It is then mixed with 50 c.c. of hydrochloric acid (sp. gr. 1·19) and 2 grs. of sodium hydrogen phosphite (NaH_2PO_2), and heated strongly (under the hood) until the excess of hydrochloric acid has been almost completely driven off. The contents of the flask are diluted with hot water, filtered, and the copper in the filtrate precipitated with hydrogen sulphide. The precipitate is washed first with water saturated with hydrogen sulphide, then with hot dilute sodium sulphide, and is finally dissolved in dilute nitric acid. From this solution the copper is recovered by the electrolytic method.

By the addition of sodium hydrogen phosphite, the iron is reduced to the ferrous condition, thereby preventing the separation of sulphur, which would otherwise occur during the precipitation with hydrogen sulphide:

$$Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S.$$

Likewise any arsenic present, which on treating the sample with nitric acid passes into solution as arsenic acid, is reduced at this stage to arsenious acid. The latter, on boiling with concentrated hydrochloric acid, forms arsenious chloride, which is readily lost by volatilization (*cf.* the determination of arsenic in iron ores, p. 142).

If the amount of sodium hydrogen phosphite exceeds that required for the reduction of the iron and arsenic acid, the arsenious chloride is further reduced to elemental arsenic, which is insoluble in hydrochloric acid.

The object of washing the precipitate of the copper sulphide with sodium sulphide is to remove any remaining traces of arsenic (or antimony) which otherwise, on electrolysis, would be deposited with the copper.

The determination of copper is important, since if any considerable amount be present its recovery from the roasted ore is profitable. Pyrites from the Rio Tinto district of Spain is especially rich in copper, containing on an average 2 to 3 per cent., and occasionally as much as 4 to 5 per cent. of this element.

Cupriferous pyrites is not roasted completely, but a certain amount of sulphur, somewhat in excess of that corresponding to the copper present, is left in. The roasted material is then mixed with common salt and calcined in air. Under these conditions the copper sulphide is oxidized to sulphate; this reacts with the sodium chloride, forming sodium sulphate and cupric chloride, which are easily leached out with water.

Occasionally the amounts of zinc and arsenic in pyrites are also determined. The Westphalian pyritic ores contain from 6 to 19 per cent. of zinc. As zinc sulphide, on roasting, is mainly converted into sulphate, the presence of zinc diminishes the amount of sulphur available. The roasted ores are also unsuitable for iron-smelting. Zinc, like copper, is removed by submitting the ore to a " chloridizing " roast.

For the determination of zinc in pyrites the filtrate from the copper determination may be used. It is boiled to expel the hydrogen sulphide, oxidized with nitric acid, and the iron precipitated as basic acetate. After filtering, the zinc in the solution is estimated either by titration, as in the case of blende (p. 167), or gravimetrically as sulphide.

The amount of arsenic in pyrites varies from about 0·5 per cent. to the merest trace. Arsenic is a very pernicious constituent; the volatile trioxide (As_2O_3) formed on roasting is only partially retained in the dust chambers; some of it passes over in the roaster gases and contaminates the sulphuric acid or other ultimate product.

For the determination of arsenic, 5 to 10 grs. of the sample are dissolved in 30 per cent. nitric acid, as described under (2), and evaporated to dryness. A few cubic centimetres of dilute sulphuric acid are added and the mixture heated on a sand-bath until thick white fumes appear. The residue is mixed with concentrated hydrochloric acid and ferric chloride, and the resulting arsenious chloride distilled off (see determination of arsenic in iron ores, p. 142).

The extensive deposits of pyrites in Spain and Portugal are of exceptionally high quality, containing 46 to 50 per cent. of sulphur. Large deposits also occur in France, North America, Germany, Norway, Hungary, and Italy. A feature of French and American pyrites is the almost complete absence of arsenic, while the German pyritic ores generally contain considerable quantities of zinc and very little copper.

In preparing the pyrites for use, the large lumps are reduced to about the size of an egg, either by hand or in mechanical crushers; the coarse material is then separated from the fine by screening, the two grades requiring different types of furnaces for roasting. Lump pyrites is roasted in hearth furnaces, the material resting on a grate of firebars, between which the air-supply is admitted. The bars are square in section, and are capable of being turned on their axes.

Once kindled, the pyrites continues to burn, since the reaction

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

furnishes sufficient heat to maintain the temperature of the mass. When the under layer of the ore is sufficiently roasted, the firebars are turned and shaken, causing a portion of the material to fall into the pit below; the new charge of ore introduced from above is fired by the glowing residue of the previous charge.

The furnaces used for roasting fine pyrites consist of a series of iron shelves arranged vertically in steps; the ore is gradually raked downwards, either by hand, as in the old

Malétra burner, or by mechanical means, as in the more recent Herreshoff furnace, while a current of air passes in the opposite direction up the shaft. The fines also continue to burn once the furnace has been heated up. The gases from the roaster, after passing through dust chambers, are used for the manufacture of sulphuric or sulphurous acid.

They usually contain a considerable amount of sulphur trioxide, owing to the fact that the iron oxide of the roast acts catalytically, promoting the union of the sulphur dioxide with oxygen. In the manufacture of sulphuric acid this is an advantage, but for sulphurous acid it is undesirable.

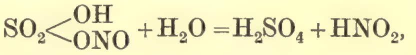
Other raw materials used for the production of sulphur dioxide are *zinc blende* (p. 167), *brimstone,* the *sulphur* recovered from spent oxide (p. 70) and residues from the Leblanc soda process (p. 104). Brimstone, formerly the only raw material employed, has been largely supplanted by the less expensive pyrites and is now used only in a few factories where a product absolutely free from arsenic is made.

7. NITROSO-SULPHURIC ACID.

1. Determination of Nitrous Acid (Lunge's Method).—The sample is run slowly from a burette (provided with a glass stopcock) into a measured quantity of standard potassium permanganate solution heated to about 40° C. until the colour of the permanganate is discharged. During the titration the solution should be stirred briskly. According to the amount of nitrogen oxides present, from 20 to 100 c.c. of 1/5 normal permanganate should be measured out and diluted with an equal volume of water.

The result is expressed in grams of N_2O_3 per litre.

Nitroso-sulphuric acid is decomposed by aqueous permanganate, with the formation of sulphuric and nitrous acids,



$$SO_2<\begin{matrix}OH\\ONO\end{matrix} + H_2O = H_2SO_4 + HNO_2,$$

the latter of which is then oxidized to nitric acid.

The object of running the acid into the permanganate, as in the titration of nitrites, is to ensure the immediate oxidation of the nitrous acid liberated, and for the same reason the permanganate solution is heated. This precaution is necessary, since nitrous acid readily decomposes, according to the equation

$$3HNO_2 = HNO_3 + H_2O + 2NO,$$

the nitric oxide thus formed escaping unoxidized from the solution.

2. Determination of Total Nitrogen Acids (Lunge's Method).—For this purpose the nitrometer shown in Fig. 21 is used. It consists of a measuring vessel *A*, terminating upwards in a small funnel, and provided with a three-way cock. This vessel is connected through a piece of thick-walled rubber tubing with the levelling tube *B;* the apparatus is charged with mercury.

According to the concentration of the sample, from 0·5 to 5 c.c. of nitroso-acid is run into the funnel from a pipette, graduated in hundredths (or from a burette having a glass stopcock), and drawn into *A* by gradually lowering the reservoir, taking care to prevent the admission of air. The acid remaining in the funnel is washed down twice with about 2 c.c. of pure concentrated sulphuric acid. The burette is then detached from the stand and shaken for two or three minutes in an almost horizontal position. The nitrogen compounds present are decomposed quantitatively by mercury in presence of sulphuric acid, with evolution of nitric oxide, according to the equations

$$N_2O_3+2Hg+H_2SO_4=Hg_2SO_4+H_2O+2NO,$$

and

$$2HNO_3+6Hg+3H_2SO_4=3Hg_2SO_4+4H_2O+2NO.$$

The gas in the burette is now brought under atmospheric pressure. Since the specific gravity of mercury is about 6·5 times that of concentrated sulphuric acid, for every 6·5 mm. of acid in the measuring limb the mercury column in the levelling tube must be set 1 mm. above that in the burette. After waiting until the apparatus has acquired a uniform temperature, the temperature, together with the barometric pressure and the volume of the nitric oxide, are noted. From the volume of gas thus obtained is deducted that of the nitric oxide calculated from the permanganate titration (1), and the remainder is calculated to grams of HNO_3 per litre of the nitroso-sulphuric acid.

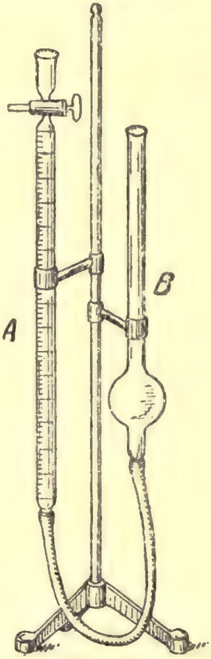


Fig. 21.

After the experiment the gas and sulphuric acid are expelled from the burette through the side opening of the three-way cock by raising the mercury reservoir; the apparatus is then ready for a new determination.

To reduce the volume of the gas to 0° and 760 mm. the well-known equation

$$V_0 = \frac{pv \times 273}{760 \times (t + 273)}$$

is used. Since the gram-molecular weight of a perfect gas occupies 22,400 c.c. at N.T.P., the weight of the corrected volume of gas found will be

$$= \frac{V_0 \times M}{22400} \text{ grs.,}$$

where M is the molecular weight of the gas in question.

Example: The volume of nitric oxide obtained in an analysis was 87·4 c.c., temperature = 21° C., barometer = 750 mm.

Reducing to N.T.P., we find

$$V_0 = \frac{750 \times 87{\cdot}4 \times 273}{760 \times 294} = 80{\cdot}1 \text{ c.c.}$$

The molecular weight of nitric oxide = 30, and the weight of 80·1 c.c. will thus be

$$= \frac{80{\cdot}1 \times 30}{22400} = 0{\cdot}1073 \text{ gr.}$$

When a number of successive experiments are made, during which the temperature and pressure remain unchanged, it is more convenient, instead of reducing the gases every time to N.T.P., to calculate once for all the volume of a gram-molecule of the gas under the prevailing conditions; for instance, if the temperature is 21° C. and the pressure 750 mm., we find that the volume of a gram-molecule at 0° and 760 mm. is equal to

$$\frac{22400 \times 294 \times 760}{273 \times 750} = 24{,}450 \text{ c.c.}$$

The weights of the individual (uncorrected) volumes of nitric oxide found are then

$$= \frac{\text{volume of gas} \times \text{molecular weight}}{24450}.$$

Lunge has devised an apparatus which enables the volume of the gas to be reduced mechanically to 0° and 760 mm. independently of the prevailing temperature and pressure. The Lunge gas volumeter, in which mercury is used, is shown in Fig. 22. A graduated tube *C*, provided with a gas-tight stopcock, is introduced between the vessels *A* and *B*. This tube is filled once for all with 100 c.c. of air at 0° C. and 760 mm. If now, by adjusting the levelling tube, the volume in the compensating vessel is brought to exactly 100 c.c. at the prevailing temperature and pressure, the volume of the gas in the burette is simultaneously reduced to 0° and 760 mm. Generally the analysis is not performed in the volumeter itself, but the gas is first generated in the ordinary nitrometer described under (2)—which in this case need not be graduated—and is then transferred to the burette, where the volume is measured as already described.

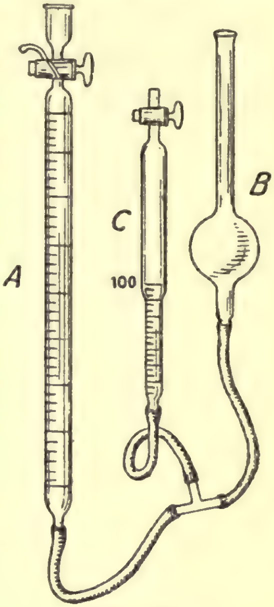


FIG. 22.

Nitroso-sulphuric acid is an intermediate product in the manufacture of sulphuric acid by the Chamber process. The gases containing nitrogen oxides, after leaving the lead chambers, are usually passed through two Gay-Lussac towers in series. These are high towers constructed of sheet lead, filled with a porous material, generally coke, down which trickles cold sulphuric acid (sp. gr. 60° to 62° Bé) distributed as uniformly as possible over the whole column, thus ensuring intimate contact with the ascending gases. The gases entering the tower should be cool, and should not contain much moisture, in order that the acid may not be unduly heated or diluted, since both these conditions are unfavourable to the absorption.

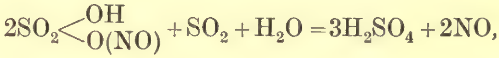
Sulphuric acid absorbs nitrogen oxides, forming nitroso-sulphuric acid, $SO_2<{OH \atop O(NO)}$, or a mixture of this with nitric acid, according to the equations—

$$(1)\quad NO + NO_2 + 2H_2SO_4 = 2SO_2<{OH \atop O(NO)} + H_2O;$$

$$(2)\quad 2NO_2 + H_2SO_4 = SO_2<{OH \atop O(NO)} + HNO_3.$$

If the amount of nitric oxide (NO) in the gases exceeds that of nitrogen peroxide (NO_2)—*i.e.*, if there be a deficiency of oxygen—a small quantity of the nitric oxide remains unabsorbed. Any nitrous oxide (N_2O) formed in the chambers is neither oxidized nor absorbed by sulphuric acid, but goes to waste. The acid flowing from the Gay-Lussac tower thus consists of a solution of nitroso-sulphuric acid in concentrated sulphuric acid, and may also contain a certain amount of nitric acid. According to Lunge, the amount of nitric acid is small, even when the gases originally contained excess of nitrogen peroxide, owing to the reducing action of the coke in the Gay-Lussac tower.

The denitration of the nitroso-sulphuric acid takes place in the Glover tower, which is installed behind the dust chambers, between the pyrites burners and the lead chambers. This is similar in shape and construction to the Gay-Lussac, but the sheet lead is protected by a lining of refractory and acid-proof material, such as quartz or earthenware, the charge likewise consisting of fragments of the same material. The nitroso-sulphuric acid, mixed with chamber acid of about 50° Bé, is allowed to flow down the tower, where it meets the ascending hot gases from the roasters, which have a temperature of about 300° C. It undergoes reduction according to the equation



$$2SO_2{<}^{OH}_{O(NO)} + SO_2 + H_2O = 3H_2SO_4 + 2NO,$$

the nitric oxide thus liberated passing forward into the lead chambers. At the same time the denitrated acid is concentrated to about 62° Bé, while the gases are cooled to the proper temperature for admission to the lead chamber.

8. FUMING SULPHURIC ACID—OLEUM.

Determination of Free SO_3—(*a*) *Indirect Method.*—Before taking the sample, the crystalline or partly crystalline oleum is liquefied by warming gently to 30° to 35° C. on a sand-bath. Oleum containing over 70 per cent. SO_3, or pure sulphuric anhydride, must not be heated, but dissolved in pure concentrated sulphuric acid. A few crystals of the solid oleum, or sulphuric anhydride, are weighed in a closed weighing-bottle; a quantity of concentrated sulphuric acid (of known strength), sufficient to give a uniform product, containing about 60 to 70 per cent. SO_3, is then added, and the mixture reweighed. Small portions of the sample thus obtained are taken for titration. A number of fragile bulbs 1 to 1½ cm. in diameter, with fine capillary tubes (4 to 6 cm. in length) on both sides, are blown from a piece of soft glass tubing. Each bulb is weighed separately and then filled with oleum by gentle suction from a pump, with which it is connected by a piece of narrow-bore pressure tubing. The liquid is removed from the lower capillary by tapping gently, the bulb carefully wiped with filter-paper and the ends of the capillaries sealed in the tip of the blowpipe. The sealed bulb is weighed, placed in a thick-walled stoppered bottle containing 200 to 300 c.c. of water, and broken by shaking violently. After waiting until the white fumes of sulphuric acid have been completely absorbed, the contents of the bottle are washed into a 500 c.c. measuring-flask, which is then filled up to the mark; 200 c.c of the solution are titrated with 1/10 normal iodine for the determination of sulphurous acid, and 200 c.c. with 1/5 normal caustic soda for SO_2+total SO_3.

If the material to be analyzed be an oleum containing less than 60 per cent. free SO_3, the Lunge-Rey glass-tap pipette shown in Fig. 23 may be conveniently employed. This consists of a bulb pipette with two glass stopcocks and a guard tube connected by a ground-glass joint. All joints should fit perfectly without grease.

The whole apparatus is weighed. The guard tube is next removed. With the lower stopcock closed, a partial vacuum is created in the bulb by gentle suction and the upper stopcock then turned to prevent access of air.

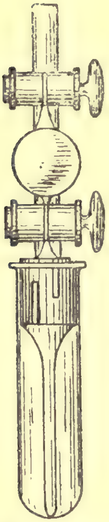


FIG. 23.

The point of the pipette is now dipped into the oleum, which, upon cautiously opening the lower stopcock, is drawn into the hollow space above, care being taken that none enters the bulb itself. The stopcock is then closed, the tube wiped with filter-paper, the guard replaced and the whole apparatus reweighed. The guard tube is once more detached and the point of the pipette immersed in water, into which the oleum is allowed to flow slowly by opening first the upper stopcock, and then very gradually the lower. After carefully washing out the pipette and guard tube with water, the whole is made up to 500 c.c., of which 200 c.c. are taken for titration as before.

The amount of free sulphuric anhydride is calculated in the following way: The volume of caustic soda solution corresponding to the sulphurous acid found in the first titration is deducted from that of the alkali used in the second titration. It should be noted that the result obtained in the titration depends upon the choice of indicator. Methyl orange indicates neutrality when the sulphurous acid has been converted into sodium hydrogen sulphite, $NaHSO_3$, whereas with phenolphthaleïn the end-point is given when the acid has been *completely* neutralized. Hence for every 1 c.c. of 1/10 normal iodine solution required, only 0·25 c.c. of 1/5 normal caustic soda should be deducted in the first case and in the latter 0·5 c.c. From the residual volume of soda the percentage of sulphuric acid is calculated, and since the *free* SO_3 is here reckoned as hydrate, the result must exceed 100 per cent. Now, 1 molecule of water

(M.W.=18) corresponds to 1 molecule of SO_3 (M.W=80); hence the surplus, multiplied by $\frac{80}{18}$ or 4·444, gives the percentage of free SO_3.

Example : An analysis gave 0·7 per cent. SO_2 and 108·6 per cent. H_2SO_4, showing a total surplus of 9·3 over 100. The percentage of free SO_3 is $9{\cdot}3 \times 4{\cdot}444 = 41{\cdot}3$ per cent.

Hence the oleum consists of—

0·7	per cent.	SO_2.
41·3	,,	SO_3.
58·0	,,	H_2SO_4.

The method just described, like all indirect methods, possesses the disadvantage that any error in the direct estimation of one of the constituents is multiplied in the indirect calculation. Moreover, in an indirect determination the assumption is always made that no substances are present other than those allowed for in the calculation. In the analysis of oleum given above, the difference between 100 per cent. and the sulphurous and sulphuric anhydride found is supposed to be H_2O. Accurate results are only to be expected when the sample is quite free from impurities. Where this is not the case, the determination of the amount of impurities present by distilling, collecting, and weighing them has been recommended; but this method would appear to be of doubtful value, since, in the first place, it is tacitly assumed that the impurities distil unchanged, which is unlikely; and, secondly, the quantitative determination of the various substances contained in the distillate is necessary.

A *direct* method for determining the free sulphur trioxide, which is especially useful in the case of very impure oleum, is the following:

(*b*) *Direct Determination of Free* SO_3 (*Setlik-Rabe Method*).—50 to 100 grs. of oleum are weighed in a long-necked flask on an ordinary balance (sensitive to 0·1 gr.). A 50 to 60 per cent. solution of pure sulphuric acid (the concentration and specific gravity of which have been accurately determined beforehand) is then slowly added from a burette, with constant shaking. If the oleum be very concentrated, cooling is necessary; the temperature should be kept below 40°. As long as any free sulphur trioxide is present, a drop of aqueous sulphuric acid falling into it produces a white cloud. Towards the end of the reaction the flask must be shaken after the addition of every drop until the fumes have completely disappeared, so that the effect of the next drop can be clearly observed. The operation is finished when a drop falling on the surface of the solution no longer produces fumes and no cloud formation takes place on blowing into the flask.

The free sulphur trioxide is calculated as before. Every gram of water which has been added with the sulphuric acid corresponds to 4·444 grs. free SO_3.

Fuming sulphuric acid, generally called *oleum,* from its old name *Oleum vitrioli,* is prepared by passing sulphur trioxide into anhydrous sulphuric acid. At ordinary temperatures it is a liquid or a crystalline solid according to the amount of SO_3 contained in it.

As shown in the diagram (Fig. 24), the melting-point curve for oleum exhibits two minima (eutectics), one at −12° C. corresponding to 16 per cent. SO_3; the second at 0°, corresponding to 61 per cent. SO_3. At 20°, as may be seen from the curve, an oleum is solid only when it contains either about 30 to 50 per cent. SO_3, or about 80 per cent. of SO_3. The pure mono-

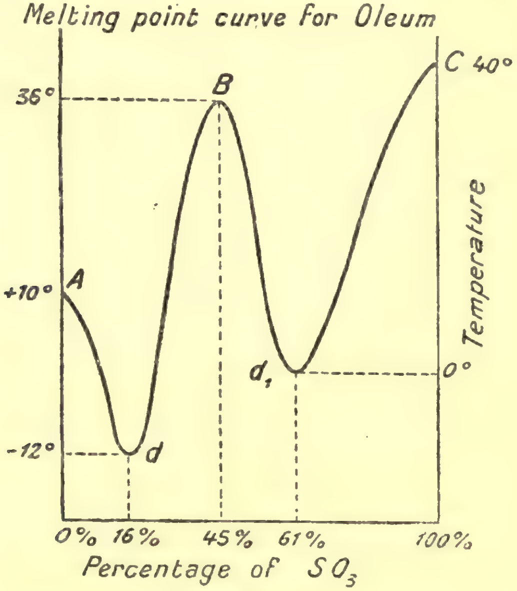


FIG. 24.

hydrate, H_2SO_4, melts at $+10°$ C., pure SO_3—*i.e.*, the more stable polymerized form—at 40°. The highest point in the middle of the curve at 45 per cent. SO_3 corresponds to the compound $H_2SO_4 + SO_3 = H_2S_2O_7$, pyrosulphuric acid, which melts at 36°. On cooling any mixture containing between 16 and 61 per cent. of free SO_3, crystals of pure $H_2S_2O_7$ separate out. The complete diagram is to be interpreted in the following way:

The lines *Ad* and *Bd* represent the depression of the freezing-point of H_2SO_4 by $H_2S_2O_7$, or of $H_2S_2O_7$ by H_2SO_4, and the lines Bd_1 and Cd_1 the depression of the freezing-point of $H_2S_2O_7$ by SO_3, or of SO_3 by $H_2S_2O_7$.

Oleum was prepared commercially as early as the sixteenth century. Argillaceous schist containing pyrites, such as occurs in the Hartz Mountains and Bohemia, was weathered for several years by exposing it in heaps, the pyrites being converted into ferrous and ferric sulphate by the combined action of water and atmospheric oxygen. These salts were leached out with water and evaporated; the vitriol thus obtained was distilled in small earthenware retorts at the highest temperature attainable. Decomposition takes place according to the equations

$$\begin{aligned}Fe_2(SO_4)_3 &= Fe_2O_3 + 3SO_3,\\ 2FeSO_4 &= Fe_2O_3 + SO_3 + SO_2.\end{aligned}$$

The mixture of SO_3 and SO_2 distilling over was collected in concentrated sulphuric acid, while the "caput mortuum"—as the residue left in the retort (red Fe_2O_3) was called—was used as a pigment. The development of the contact process led to the decline of this old industry, which is now obsolete. In the new process sulphur trioxide is prepared by the oxidation of sulphur dioxide with oxygen. The synthesis and decomposition of sulphur trioxide are represented by the reversible equation

$$2SO_2 + O_2 \rightleftharpoons 2SO_3.$$

When this reaction proceeds from left to right, 45·2 Cals. of heat are liberated, and the same amount is absorbed in the reverse reaction.

According to van't Hoff's rule, all reversible reactions proceed towards the endothermic side when the temperature is raised, and towards the exothermic when the temperature is lowered; hence, other conditions being identical, the concentration of sulphur trioxide in presence of sulphur dioxide and oxygen will decrease with rising temperature and increase as the temperature falls, while if the temperature be kept constant, the concentration of the individual components taking part in the reaction is governed by the law of Mass Action—

$$K = \frac{[C_{(SO_3)}]^2}{[C_{(SO_2)}]^2 \times C_{(O_2)}}$$

or

$$C_{(SO_3)} = K.C_{(SO_2)}.\sqrt{C_{(O_2)}},$$

where $C_{(SO_3)}$, etc., represent the concentration of SO_3, etc.

Fig. 25 shows graphically the maximum theoretical yield of sulphur trioxide obtainable at various temperatures. The values represented by the continuous curve are those obtained when the gases are mixed in combining proportions—*i.e.*, 2 vols. of sulphur dioxide with 1 vol. of oxygen; while those on the broken curve

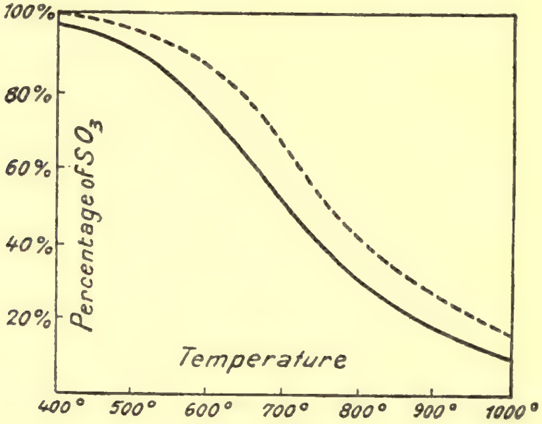


FIG. 25.

are obtained with a mixture containing excess of oxygen—viz., 1 vol. sulphur dioxide and 2 vols. of oxygen. The amount of sulphur trioxide obtained is less in the first case than in the second, in accordance with the law of Mass Action. The diagram also shows that up to about 400° C. the system is in equilibrium on the SO_3 side; hence at and below this temperature the reaction, which in the absence of a catalyst proceeds extremely slowly even at 800° to 900° C., must be accelerated catalytically if the quantitative combination of sulphur dioxide and oxygen is to be realized.

The fact that platinum black (spongy platinum), which is an active catalyst in so many instances, is also effective in promoting this reaction had long been known, but Clemens Winkler was the first to succeed in producing sulphuric anhydride on a large scale by the use of platinum as contact substance. The results obtained were so excellent that the contact process may justly be called "Winkler's process." He passed roaster gases—*i.e.*, sulphur dioxide mixed with excess of air*—over fragments of platinized unglazed porcelain heated to 440° to 460° C. in cast-iron retorts and obtained a yield as high as 97 per cent. of SO_3. After Winkler had observed that the activity of the contact substance was very quickly diminished by the dust contained in the roaster gases, he submitted the latter to careful purification by passing them first through leaden dust chambers and then through a series of lead towers filled successively with coke, charcoal, fine wood shavings, and cotton-wool. The essential features of the process were thus completely established. The investigation of the physico-chemical details of the process is due to Knietsch, who also discovered that arsenic is the constituent of flue dust, which is most pernicious in "poisoning" the activity of the platinum, and emphasized the importance of its complete removal. Knietsch's process, as worked by the Badische Anilin- und Soda-fabrik, does not differ essentially from that of Winkler. The newer process of Clemm and Hasenbach introduced at the Verein chemischer Fabriken at Mannheim is original. In this the gases are passed first over roasted pyrites residue heated to 600° to 700° C., which is the next best catalyst to platinum; with iron oxide, however, the reaction reaches its maximum efficiency at 600°, at which temperature only 60 to 70 per cent. of the sulphur dioxide is converted into trioxide. The latter is absorbed in sulphuric acid and the gases are then conducted through the platinum catalyst at 400° C., by which the oxidation of the remaining sulphur dioxide is completed. A great advantage of this process, apart from the economy of platinum, is that the roaster gases need not be purified before use, since the iron oxide itself retains the arsenic as iron arsenate.

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* See Lunge, "Sulphuric Acid and Alkali," vol. i., p. 984 (1903).

9. CHILE SALTPETRE.

1. Determination of Nitrate—(*a*) *Devarda's Reduction Method.*—20 grs. of the sample are dissolved in 1,000 c.c. of water; 25 c.c. of this solution are transferred to an Erlenmeyer flask of about 1 litre capacity, diluted with water to 300 c.c. and mixed with 5 c.c. of alcohol, 2 grs. of Devarda's alloy and 20 c.c. of 25 per cent. caustic soda solution. The flask is then connected through an air condenser with a vessel containing a measured volume of 1/5 normal sulphuric acid (Fig. 26). After standing for one hour, during which the greater portion of the nitrate is reduced to ammonia, the Erlenmeyer flask is heated carefully until the alloy has been completely decomposed.

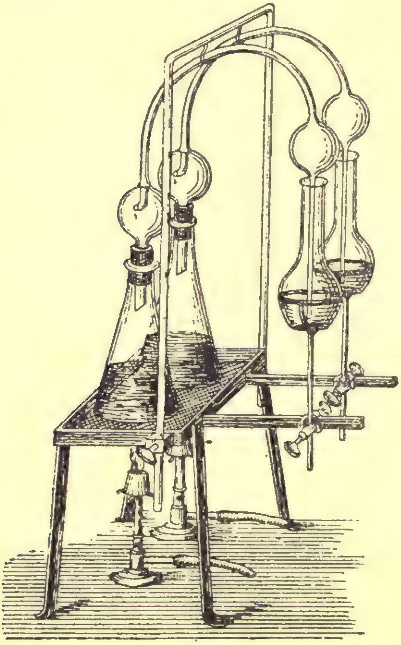

Fig. 26.

Finally, the solution is boiled for about half an hour to expel the ammonia. The sulphuric acid in the receiver is allowed to cool, and then titrated with 1/5 normal caustic soda, using methyl orange as indicator.

Devarda's metal, consisting of an alloy of aluminium, zinc, and copper, is particularly suitable for the rapid quantitative reduction of nitrates to ammonia. The direct reduction is due to the aluminium and zinc, which form with the less electro-positive copper innumerable small galvanic elements in which the nitrate plays, as it were, the rôle of depolarizer. The efficiency of this alloy is further increased by the fine state of division in which it is used, its extreme friability rendering it easy to prepare in this form.

In titrating the excess of sulphuric acid, phenolphthaleïn cannot be employed as indicator, owing to the presence of ammonium salts.

(*b*) *Volumetric Method* (*Schloesing-Grandeau-Wagner*).—A round-bottomed 300 c.c. flask is fitted with a rubber stopper, through which pass the stem of a tap funnel (of about 15 c.c. capacity) and a bent tube for leading off the gases (Fig. 27). The stem of the funnel, which should not extend more than half-way down the neck of the flask, is narrowed at the end. The delivery tube leads from the flask into a trough filled with freshly boiled water.

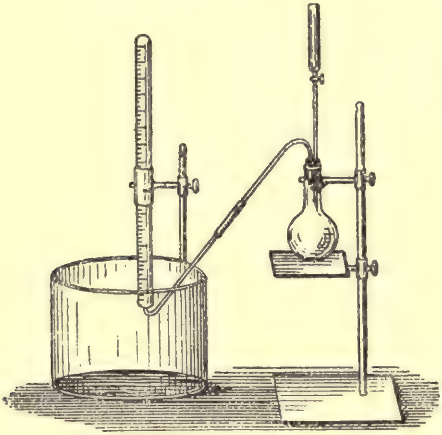

FIG. 27.

40 c.c. of a 25 per cent. solution of ferrous chloride are run into the flask, the stopper inserted and 40 c.c. of 20 per cent. hydrochloric acid added through the funnel, taking care that some of the acid remains in the tube below the stopcock. The mixture is boiled until the air has been completely expelled from the apparatus. A 100 c.c. measuring tube, graduated in tenths, is now clamped in a vertical position over the end of the delivery tube and, without interrupting the boiling, 15 c.c. of a solution con-

taining 20 grs. of chemically pure sodium nitrate per litre (or an equivalent amount of potassium nitrate) are run in slowly from the funnel. The funnel is then washed out twice with 20 per cent. hydrochloric acid, and the boiling continued until the evolution of gas has ceased. The tube containing the gas is then transferred to a deep cylinder filled with water and replaced by a second collecting tube. During this operation the ferrous chloride solution, which suffices for a large series of experiments, must be kept boiling; 15 c.c. of a solution containing 20 grs. of the sample per litre are then poured into the funnel and the experiment repeated. If a sufficient number of collecting tubes are available, one or two additional determinations may be made with this solution, after which the pure nitrate solution is tested a second time. The cylinder containing the measuring tubes is allowed to stand for about fifteen minutes to acquire a uniform temperature; the tubes are then adjusted until the water inside and out is at the same level and the volumes of gas collected are noted. These volumes, without any correction, are directly proportional to the percentage of nitrate in the dissolved substances.

Nitre, on boiling with a solution of ferrous chloride in hydrochloric acid, is reduced quantitatively to nitric oxide, which, being practically insoluble, can be collected over water:

$$NaNO_3 + 3FeCl_2 + 4HCl = NaCl + 3FeCl_3 + 2H_2O + NO.$$

The slight error arising from the absorption of a small quantity of nitric oxide is eliminated by making a blank experiment under the same conditions.

Besides the two methods just described, several others are employed in technical practice, the most important of which are the following:

(1) *Methods of Reduction of Ammonia.*—Instead of reducing with Devarda's metal, the old method of reduction in alkaline solution with zinc and iron dust may be used, but this is tedious.

The nitrate may also be reduced in acidic solution to ammonium salts, which are then distilled with excess of alkali. In this case reduction is effected in sulphuric acid either with iron dust (Ulsch), or by electrolysis, using a copper-plated platinum cathode (Vortmann), or in concentrated phenyl-sulphuric acid with zinc dust (Iodlbauer).

(2) *Methods of Reduction to Nitric Oxide.*—The reduction of nitre to nitric oxide can be accomplished either by boiling with acid ferrous chloride (as in Schloesing's method), or by treatment with mercury and concentrated sulphuric acid in the Lunge nitrometer, as described on p. 78. In Pelouze's method the nitre is reduced with a measured volume of a solution of ferrous chloride or sulphate of known strength and the excess of iron titrated back with permanganate. If ferrous sulphate be used, the reduction is quantitative only when the concentration of the sulphuric acid solution exceeds about 30 per cent.

2. Determination of Chloride and Perchlorate.—(*a*) *Chloride.*—4 grs. of the sample are dissolved in water and titrated with decinormal silver nitrate, using a few drops of neutral potassium chromate solution as indicator.

(*b*) *Perchlorate.*—5 grs. of the sample, contained in a large platinum crucible, are moistened with concentrated sodium carbonate solution and stirred together with 0·5 gr. of finely powdered manganese dioxide free from chloride. The mixture is heated in the covered crucible at dull redness for thirty minutes.

After cooling, the sintered mass is dissolved in hot water and washed into a 250 c.c. flask. The solution is just acidified with nitric acid, then mixed with a slight excess of precipitated calcium carbonate (free from chloride) and the whole diluted with water to the mark; 200 c.c. of this solution, passed through a *dry* filter, are titrated with silver nitrate, with the addition of potassium chromate as before, and, after deducting the volume of silver nitrate required in (*a*), the amount of perchlorate is calculated and expressed as $KClO_4$.

Perchlorates, on heating, are converted into chlorides, with liberation of oxygen. The decomposition is greatly accelerated by the presence of manganese dioxide, which acts as a catalyst (laboratory method of preparing oxygen). Sodium carbonate is added to decompose any magnesium chloride present, since this, on heating, readily decomposes, with the formation of hydrochloric acid.

Chile saltpetre generally contains also a small quantity of chlorate, which on heating is converted first into perchlorate and then into chloride. Chlorate (as also iodate, which may be present in exceptional cases) is rarely determined separately, but is usually returned with the perchlorate. Analytically chlorate is easily distinguished from perchlorate by the fact that it can be reduced quantitatively by such agents as zinc dust and ferrous sulphate, even in aqueous solution, while perchlorate is not attacked.

In the preparation of nitric acid from saltpetre by treatment with sulphuric acid, any chloride present is decomposed, with the formation of hydrochloric acid; this is immediately oxidized to chlorine, which remains as an impurity in the nitric acid. Chlorine is also produced from perchlorate, since the perchloric acid ($HClO_4$) primarily formed is extremely unstable in the anhydrous condition and rapidly decomposes. The chlorate also, which on ordinary treatment with concentrated sulphuric acid forms explosive chlorine peroxide, ClO_2, yields only chlorine under the prevailing conditions of this process.

The presence of chloride in Chile saltpetre, used as a fertilizer, is of little consequence, but any considerable amount of perchlorate is objectionable, since this salt is injurious to vegetation. Not more than 1·5 per cent. of potassium chlorate is permissible. Rye is especially sensitive to this substance.

Sodium nitrate, commonly known as Chile saltpetre, from the country in which it is chiefly obtained, occurs in extensive deposits over the central portions of the rainless west coast of South America. The most productive localities are near the coast, extending from about Pisagua to south of the desert of Atacama, mostly at an altitude of 2,500 to 5,000 feet above sea-level. The stratum of earthy saltpetre, called *caliche,* varies from 8 inches to 16 feet in thickness; it is not found on the surface, but lies beneath a layer of *costra* 20 inches to 5 feet thick, composed of a conglomerate of clay and lumps of felspar cemented to a hard mass by gypsum, sulphates of potash and soda, and sodium chloride. Beneath the caliche is a soft earth rich in sodium chloride.

The amount of saltpetre in a paying deposit varies from 20 to 70 per cent. The chief impurities are sodium chloride and sulphate, occasionally with a small percentage of potassium nitrate and perchlorate, and a little iodine, mostly in the form of iodate. The crude saltpetre is conveyed to factories in the vicinity, where it is systematically extracted with boiling water by a process of lixiviation similar to that employed in the extraction of sodium carbonate from black ash. The saturated solution of crude nitre is pumped into shallow wrought-iron tanks, where it is left for several days to crystallize. The mother-liquor is then run off and the crystals of sodium nitrate are shovelled first on an inclined draining platform covered with sheet iron, where it remains for several days, and then on to a cemented floor, where it is left to dry in the air for about fourteen days. It is then packed in sacks for export. In this way a commercial (95 per cent.) product is obtained which is generally yellowish-grey or pale red in colour, and sometimes emits a faint smell resembling iodoform, owing to the presence of a small amount of iodine. If, however, the hot solution is allowed to settle for some time before being pumped into the coolers, it is possible to obtain a perfectly white product containing 96 to 98 per cent. of sodium nitrate.

When the caliche contains much potassium perchlorate (which is the case only in a few districts), this is removed by a special treatment, based upon the fact that potassium perchlorate, although readily soluble in hot water, is almost insoluble in cold water. The solution obtained from the lixiviation of the crude material in the ordinary way is run out of the cooling-pan while still warm and the first crop of nitre crystals, which separate at this stage quite free from perchlorate, is removed. The nitre, which crystallizes on further cooling, is rich in perchlorates; it is treated with a very small quantity of cold water, which dissolves only the nitrate, leaving the perchlorate in the residue.

The mother-liquor from the crystallizing pans is used over and over again, and is finally treated for the recovery of iodine. For this purpose a solution of sodium bisulphite is added until the iodine, which is liberated according to the equation

$$4NaIO_3 + 10NaHSO_3 = 2I_2 + 7Na_2SO_4 + 3H_2SO_4 + 2H_2O$$

begins to redissolve:

$$I_2 + NaHSO_3 + H_2O = 2HI + NaHSO_4.$$

The iodine settles out in the form of a black mud, which is recovered in a filter-press. It is purified by sublimation in iron retorts and packed for export in small wooden casks coated inside with paraffin wax or pitch. The Chilean nitre works supply the greater portion of the iodine of commerce and are capable of satisfying the demands of the world's markets.

Many hypotheses have been put forward to account for the unique mode of occurrence of saltpetre, but none offers a complete explanation of all the facts. According to Nöllner, the saltpetre-bearing coastal zone represents the old sea floor, which has been slowly elevated for a long period. The formation of saltpetre, contaminated with sodium chloride and iodine, is due to the subsequent decomposition of seaweed cast up and stranded in enormous quantities by the storm tides. Ochsenius attributes the origin of nitrate to ammoniacal dust carried by the wind from guano deposits along the coast. The production of nitrate by the discharge of atmospheric electricity has also been offered as a possible explanation. (W. Newton considers that the deposits result from a local concentration of nitrates, originally formed by the oxidation of organic matter in alluvial soil, which have been leached out of wide areas by occasional floods.—*Tr.*) Opinion is also divided in regard to the question of available reserves. While some authorities believe that at the present rate of consumption the deposits may become exhausted in thirty to forty years, the Chilean Government estimates that in the State fields alone there are 500 million tons which can be profitably extracted, while that owned by private companies greatly exceeds this amount. Consequently, Chile will be able to supply the world's demand for several centuries.

Together with the ammonia recovered from coal and sold chiefly in the form of ammonium sulphate, Chile saltpetre represents the most important source of combined nitrogen. About four-fifths of the entire output is used in agriculture, the remainder in the chemical industry for the manufacture of nitric acid, sodium nitrate, and potassium nitrate.

Within recent years the old problem of the synthetic formation of nitric oxide from atmospheric nitrogen and oxygen has been solved, and the economic production of nitrate on a large scale from this source is now an accomplished fact.

At a temperature of about 2,000° C. nitrogen and oxygen combine to form nitric oxide—

$$N_2 + O_2 \rightleftharpoons 2NO.$$

This is a reversible reaction. The formation of nitric oxide is accompanied by a large absorption of heat, amounting to 43·2 Cals. for every 2 molecules; hence the reaction in the direction from left to right is favoured by a high temperature. According to Nernst's calculation, starting with air, equilibrium is established when the percentage by volume of nitric oxide amounts to 1·2 per cent. at 2,000° C. and about 5·3 per cent. at 3,000° C. These high temperatures can only be obtained by the use of electricity, and for this reason the manufacture of synthetic nitrate is at present confined to countries possessing abundant water-power, by means of which electrical current can be cheaply generated.

The new nitrate industry was first established in Norway, where saltpetre is prepared on a large scale by two different processes.

In the process of *Birkeland* and *Eyde* a high-tension arc (4,000 to 5,000 volts) passing between water-cooled copper pipe electrodes is drawn out by means of powerful electromagnets to a flat disc of flame having a radius of about 1 metre. The temperature of the arc is estimated by Birkeland to be about 3,200° C. On blowing a strong current of air through the chamber of refractory material which encloses the arc, nitric oxide is produced to the extent of 1½ to 2 per cent. by volume.

The second process, owned by the Badische Soda- und Anilinfabrik, is due to *Schönherr*. By means of a spirally ascending current of air, the high-tension arc is drawn out to a thread 5 to 7 metres in length in a long, narrow tube of iron, which is well insulated on the outside. The percentage of nitric oxide is about the same as that obtained in the first-named process. The mixture of air and nitric oxide leaving the furnace at about 900° C. is cooled to 250° in iron cylinders, the waste heat being utilized for steam-raising. Since iron is readily attacked by the nitrous gases below 200° C., the cooling is completed in water-cooled aluminium tubes. The gases leaving these at a temperature of 40° to 50° enter a spacious " oxidation chamber," which serves to reduce the speed of flow and allows time for the nitric oxide to combine with the oxygen in the excess of air, forming nitrogen peroxide. The gases then pass through several towers constructed of granite blocks filled with pieces of quartz, where the nitrogen oxides are absorbed in a descending stream of water—

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

and

$$NO_2 + NO + H_2O = 2HNO_2.$$

The nitrous acid is either oxidized by nitric acid, or it decomposes according to the equation

$$3HNO_2 = HNO_3 + 2NO + H_2O,$$

the nitric oxide thus formed uniting with further oxygen from the air, and so on.

In this way about 70 per cent. of the nitrogen oxides present can be converted into nitric acid of approximately 40 per cent. by volume and practically free from nitrous acid. The rest cannot be absorbed by water alone; hence the gases are passed through a wash-tower of sodium carbonate solution. As the largely diluted nitric oxide is oxidized to peroxide only with difficulty, absorption takes place almost entirely in accordance with the following equation, whereby sodium nitrite is formed:

$$NO_2 + NO + Na_2CO_3 = 2NaNO_2 + CO_2.$$

A small portion of the nitric oxide, amounting to about 4 to 6 per cent., escapes oxidation and absorption and is lost in the air. The 40 per cent. nitric acid obtained in the towers is neutralized by the addition first of limestone and finally of milk of lime, and the solution evaporated until it contains about 80 per cent. of calcium nitrate. On cooling, the nitrate solidifies. It is ground to a fine powder, packed in barrels, and marketed as "lime nitrate" containing 13 per cent. nitrogen.

The process of Birkeland and Eyde has been used at Notodden since 1905. The available water-power is 40,000 h.p. In the larger factory at Saaheim, on the Rjukan, both the Birkeland-Eyde and Schönherr processes are in use. The Rjukan generating station, the largest in Europe, is supplied with about 50 cubic metres of water per second, under a head of approximately 1,000 feet, which is conveyed in ten large mains to the same number of turbo-generators, each of 15,000 h.p. Another power plant of nearly equal size is situated 900 feet lower down at Saaheim, where the same water is utilized over again.

(In the *Pauling furnace* the electrodes are inclined towards each other in the form of a V, and are separated at the bottom by a narrow space. Across this project a pair of thin metal blades, which are adjusted by means of screws until the gap between them is reduced to about 3 mm. The arc passing across this gap is forced upwards between the main electrodes by an ascending stream of preheated air from a nozzle, producing a long flame. A furnace generally consists of two or three arcs in series enclosed in a case of refractory material. These furnaces are in use in Westphalia; at Patsch, near Innsbruck; Roche-de-Dame, in the South of France; near Milan; and elsewhere.—*Tr.*)

10. BLACK ASH.

FIFTY grs. of a good average sample, rapidly ground in a mortar, are transferred to a 500 c.c. graduated flask and extracted with distilled water at 40° to 45° C. The mixture should be well shaken to prevent the formation of lumps. After cooling completely, the flask is filled to the mark and 20 c.c. more water added, to allow for the volume of the insoluble matter.

1. Determination of Total Lime.—The flask is shaken vigorously and, without allowing the solid matter to settle, 5 c.c. of the suspension are taken with a pipette (which should have an especially wide delivery). Any solid matter adhering to the outside of the stem is removed with filter-paper, after which the pipette is discharged into a 100 c.c. graduated flask and rinsed out with a small quantity of distilled water. A few cubic centimetres of concentrated hydrochloric acid are then added, and the flask heated until the carbon dioxide and hydrogen sulphide have been completely expelled. After cooling, a few drops of methyl orange are added, and the solution carefully neutralized with dilute caustic soda; 30 c.c. of $\frac{1}{5}$ normal sodium carbonate solution are then added, the mixture boiled for a few minutes and finally cooled and made up to the mark; 50 c.c. of this solution are passed through a dry filter, and the excess of sodium carbonate ascertained by titration with $\frac{1}{5}$ normal hydrochloric acid, using methyl orange as indicator. From the amount of sodium carbonate used up, the percentage of calcium carbonate in the sample may be calculated.

By the action of hydrochloric acid, the calcium compounds present, consisting chiefly of sulphide, oxide, and carbonate, are converted into chloride. On boiling the neutralized solution of calcium chloride with sodium carbonate, the whole of the calcium is precipitated as carbonate. At the same time, any iron, aluminium, and magnesium are thrown down, but the amounts of these are so small that they may be neglected, particularly as the result obtained by this method is only approximate and intended merely for the control of the working conditions.

2. Determination of Free Lime.—5 c.c. of the suspension taken as in (1) are transferred to a small beaker and mixed with an excess of barium chloride solution, followed by a few drops of phenolphthaleïn as indicator. The solution is then titrated slowly with $\frac{1}{5}$ normal hydrochloric acid, with constant stirring, until the colour is just discharged. The volume of acid required corresponds to the amount of calcium hydroxide present (or its equivalent of sodium hydroxide), *plus* one-half of the sodium sulphide; 0·25 c.c. must first be deducted for every cubic centimetre of decinormal iodine solution used in the direct titration of sodium sulphide described under (4); the residual volume is then calculated in terms of CaO.

In the titration of alkali hydroxides in presence of alkali carbonates by C. Winkler's method, excess of barium chloride is added to precipitate the carbonates as $BaCO_3$. If now, without filtering off the barium carbonate, hydrochloric acid is slowly added with constant stirring, the colour of the phenolphthaleïn is discharged when the hydroxide is just neutralized, the precipitated barium carbonate (which is neutral to phenolphthaleïn) remaining unchanged.

Sodium hydroxide is not present in the sintered mass itself. Occasionally a small amount of sodium oxide may be formed by the decomposition of sodium carbonate when the temperature of calcination is too high, but as a rule only lime is present. During the process of extraction with water, the lime reacts with the sodium carbonate more or less completely, according to the temperature and concentration of the solution, whereby calcium carbonate and sodium hydroxide are formed. The separate determination of free lime and caustic soda in the solution is therefore useless; the whole of the caustic soda should be calculated in terms of CaO.

In practice it is customary to add to the charge an excess of limestone to increase the porosity of the sintered mass. On subsequent hydration the burnt lime swells and bursts open the mass, thus facilitating the extraction (*cf.* footnote, p. 103).

Sodium sulphide, when titrated in presence of phenolphthaleïn, behaves like sodium carbonate; the colour of the indicator is discharged when the normal sulphide (Na_2S) is converted into the acid sulphide (NaHS). The end-point, however, is only sharply defined in a cold concentrated solution. In dilute or hot solutions sodium hydrogen sulphide is hydrolyzed to caustic soda,

$$2NaHS + H_2O = 2NaOH + H_2S,$$

and the titrated solution assumes a red tint on long standing, traces of hydrogen sulphide escaping at the same time.

For determinations (3), (4) and (5), test portions are taken from the clear liquid. For this purpose the flask is allowed to stand until the suspended matter has settled, or the solution may be passed through a *dry* filter.

3. Determination of Total Alkalis.—10 c.c. of the clear aqueous extract (=1 gr. black ash) are titrated in the cold with $\frac{1}{5}$ normal hydrochloric acid, using methyl orange as indicator. This gives the amount of sodium carbonate, sodium hydroxide, and sodium sulphide present. In this case the sodium sulphide (Na_2S) is titrated as a dibasic salt, and not as in (2); hence for every cubic centimetre of decinormal iodine solution used in determination (4), 0·5 c.c. of $\frac{1}{5}$ normal hydrochloric acid must be deducted. The remainder is calculated into equivalent Na_2CO_3.

The separate determination of sodium hydroxide and carbonate is valueless, as already explained under (2). The sodium hydroxide, expressed as equivalent CaO in (2), is here calculated to Na_2CO_3.

4. Determination of Sodium Sulphide.—10 c.c. of the clear aqueous extract, diluted to about 250 c.c. with water, are acidified with hydrochloric acid and titrated immediately with decinormal iodine solution.

$Na_2S + I_2 = 2NaI + S$; therefore 1 c.c. of decinormal iodine = 0·0039 gr. Na_2S.

A good product should not contain more than a trace of *sodium sulphide*. When the extraction with water is performed at too high a temperature sodium sulphide may be formed by the reaction

$$Na_2CO_3 + CaS = Na_2S + CaCO_3.$$

Of the sulphur compounds, freshly prepared black ash generally contains only sulphates and sulphides, while thiosulphates and sulphites are found after long exposure to the atmosphere (*vide infra*).

5. Determination of Sodium Sulphate.—20 c.c. of the clear aqueous extract, acidified with hydrochloric acid, are heated to boiling, and barium chloride added drop by drop until there is no further precipitation. The precipitate of barium sulphate is filtered off, burnt moist in a porcelain crucible, ignited, and weighed.

If the process of manufacture has been properly conducted, the product usually contains less than 1 per cent. of sodium sulphate, though occasionally 2 per cent. or more may be present.

6. Statement of Results.—The total sodium found is calculated into sodium sulphate, Na_2SO_4, and compared with the total lime, when it is at once seen whether the components of the charge have been mixed in the correct proportions.

The Leblanc soda process represents the earliest successful attempt to solve the problem of preparing sodium carbonate from common salt. It was devised by Leblanc in 1791 for a prize offered by the French Academy, but was first established on an industrial scale early in the nineteenth century in England. For half a century it occupied a predominant position in the soda industry; indeed, it may be said to have formed the pivot of the inorganic chemical industries, since it utilized sulphuric acid and furnished hydrochloric acid, which latter formed the raw material for the manufacture of chlorine, calcium chloride, and other chlorine compounds. With the introduction of the more economical Solvay process, the importance of the Leblanc process declined, but for a time it survived on account of the valuable by-products (hydrochloric acid and chlorine). The more recent development of the electrolytic alkali process, also yielding chlorine (from which, in turn, hydrochloric acid is readily prepared), has driven the old process almost out of existence. Only in England is any considerable quantity of Leblanc soda still manufactured. Most works either use the black ash directly for the preparation of caustic soda, or convert the salt cake into sodium sulphide, which is employed in the manufacture of sulphur colouring matters and in the tanning industry for the depilation of hides.

Outline of the Leblanc Process.—Crushed rock salt is treated with 60° Bé sulphuric acid (Glover acid) in closed leaden or iron pans provided with flues for the escape of gas. The first stage of the reaction takes place at a moderate temperature and results in the formation of sodium bisulphate and hydrochloric acid—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl \ldots\ldots\ldots (i).$$

The material is then raked into a firebrick muffle, likewise provided with an outlet for the escaping gases, and heated to 700° to 800° C. At this temperature a second molecule of salt reacts with the sodium bisulphate, forming normal sulphate—

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl \ldots\ldots\ldots (ii).$$

The sulphate (salt cake) is now mixed with excess of limestone and coal (or lignite) and the mixture heated to bright redness in a reverberatory furnace. The charge requires constant stirring. This laborious operation was at first performed with hand rabbles, but mechanically rotating cylinders (revolving furnaces) gradually came into use in the larger establishments. During the heating the following reactions[1] take place:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

A mixture of sodium carbonate with insoluble calcium sulphide, called *Black Ash*, remains, which, as already stated, should contain some free lime. In addition, it usually contains a small percentage of carbon, potassium carbonate, sodium sulphide and sodium chloride, together with traces of iron, alumina, magnesia, silica and cyanogen compounds derived from the coal.

The black ash is broken into lumps and thrown into large iron tanks, where it is extracted with water at about 50° C. on the counter-current principle. This system is commonly employed when a solution of high concentration together with an efficient extraction of a solid or absorption of a gas is required. It consists in bringing the almost exhausted material (or dilute gas) into contact with the fresh solvent, and the almost saturated solvent into contact with rich material (or concentrated gas). In the absorption of gases—*e.g.*, in the manufacture of hydrochloric acid—this is done by causing the gas and water to flow in opposite directions; hence the designation " counter-current." In the systematic extraction of solids the material is contained in a series of tanks placed side by side, and the flow of the solvent regulated correspondingly by an arrangement of stopcocks.

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[1] In the last stage of the heating, the excess of limestone and carbon reacts with the formation of carbon monoxide ($CaCO_3 + C = CaO + 2CO$) which "leavens" the pasty mass, causing it to acquire a certain porosity whereby the subsequent lixiviation is promoted.—*Tr.*

The solution of crude soda, which is always turbid, is run into clarifying tanks, where any solid matter settles out. The clear solution usually has a green colour, due to the presence of a soluble complex iron-sodium-sulphide of unknown constitution. Before the sodium carbonate is extracted the solution has to be purified; this is effected either by carbonation or oxidation, or both. The crude liquor is run down a tower charged with lumps of coke, where it meets an ascending current of air or of gas from the lime-kilns or furnaces. By the process of carbonation—*i.e.*, saturation with carbon dioxide—the caustic alkali present is converted into carbonate; the sodium sulphide is decomposed with evolution of hydrogen sulphide, which precipitates the iron previously held in solution, and the sodium aluminate and silicate are decomposed. By oxidation the sodium sulphide is converted into thiosulphate, $Na_2S_2O_3$, and the iron precipitated as oxide.

The purified lye is filtered, then concentrated in iron pans, either by top firing or bottom firing, and finally allowed to crystallize, or it may be evaporated completely to dryness and calcined. In the first case *soda crystals* (washing soda), $Na_2CO_3.10H_2O$, are obtained; in the latter anhydrous sodium carbonate, *soda ash*. In top firing the gases pass over the open pan; this method is the more economical, but the soda is to a certain extent contaminated with flue dust. Bottom firing, on account of the imperfect conduction of heat, requires more fuel; moreover, the pan is liable to crack owing to the formation of a hard crust on the bottom during the evaporation. For this reason the pans employed for bottom firing are provided with a mechanically driven rake which scrapes the bottom of the pan, breaking up the crust and pushing it over the edge into a conveniently placed strainer. These evaporators, which are extensively employed in industrial work, are called "Thélen pans," after the name of the inventor.

The insoluble residue from the black ash, consisting of calcium sulphide, carbonate, and hydroxide (alkali waste or tank waste), was formerly dumped into waste heaps, which in the course of years assumed enormous proportions and became a serious nuisance, owing to the liberation of hydrogen sulphide by weathering. Subsequently attempts were made to recover the sulphur. The Schaffner and Mond process consisted in exposing the residue to the weather for some weeks. Under the influence of air and moisture the following changes take place in the mass: The insoluble calcium sulphide is decomposed, with the formation of soluble calcium hydrosulphide and hydroxide, and part of the hydrosulphide is oxidized to calcium thiosulphate:

$$2CaS + 2H_2O = Ca(HS)_2 + Ca(OH)_2,$$
$$Ca(HS)_2 + 2O_2 = CaS_2O_3 + H_2O,$$

in addition to which polysulphides (especially the pentasulphide CaS_5), sulphites, and sulphates are formed. The mass is then extracted with water and treated with hydrochloric acid, whereby hydrogen sulphide is produced from the hydrosulphide, while the thiosulphate yields sulphur and sulphur dioxide:

$$Ca(HS)_2 + 2HCl = CaCl_2 + 2H_2S,$$
$$CaS_2O_3 + 2HCl = CaCl_2 + S + SO_2 + H_2O.$$

The hydrogen sulphide and sulphur dioxide thus formed interact, with liberation of sulphur—

$$2H_2S + SO_2 = 2H_2O + 3S.$$

By this process, assuming that the hydrosulphide and thiosulphate are present in correct proportions, the whole of the sulphur should be recovered according to the general equation

$$Ca(HS)_2 + CaS_2O_3 + 4HCl = 2CaCl_2 + 3H_2O + 4S.$$

The amount of sulphur recovered in practice was, however, only 50 to 60 per cent. of that calculated. It was purified from the sand and gypsum present by melting.

The increasing cost of hydrochloric acid rendered this process unprofitable, and it was replaced by that of Chance and Claus.

In this process the residue is agitated with water and treated in tall cylinders with carbon dioxide, by which the whole of the sulphur is liberated as hydrogen sulphide:

$$2CaS + H_2O + CO_2 = CaCO_3 + Ca(HS)_2,$$
$$Ca(HS)_2 + H_2O + CO_2 = CaCO_3 + 2H_2S.$$

The hydrogen sulphide is then mixed with the calculated quantity of air and passed over ferruginous bauxite heated to redness, whereby it is oxidized to sulphur and water—

$$2H_2S + O_2 = 2H_2O + 2S.$$

Small quantities of black ash residues are still used in the preparation of sodium thiosulphate, $Na_2S_2O_3.5H_2O$. This is obtained from the calcium thiosulphate formed on oxidation by treating it with sodium carbonate or sulphate and filtering from the residual calcium carbonate or sulphate.

11. AMMONIA SODA PROCESS.

A.—Raw Material.

I. Ammonium Sulphate.

1. Determination of Moisture.—5 grs. of the sample are dried at 110° C. for two hours, and the loss determined.

2. Determination of Ammonia (Volumetric Method by Means of the Knop-Wagner Azotometer).—The method consists in oxidizing the ammonia to nitrogen by treatment with sodium hypobromite.

A weighed amount of ammonium sulphate, dissolved in water, is placed in the tube *a* fused to the base of the wide-necked bottle *A*, and an excess of alkaline hypobromite (*vide infra*) is run into the space around the tube (Fig. 29). After inserting the stopper (through which passes an outlet tube), the bottle is immersed in cold water in the trough *B*.

The stopcock *c* is loosened and, by manipulating the rubber ball *g*, the levelling tube *e* and the burette *d* are filled with water through *f*. By carefully reopening the tap *f*, the meniscus in the burette is adjusted to zero. After waiting about ten minutes for the apparatus to acquire a uniform temperature, the stopcock *c* (previously well greased) is pressed home, but still left open. If after standing for a further five minutes the meniscus remains at zero, the experiment can be started; should the water-level have changed, the stopcock *c* is again loosened, the level re-adjusted, and the stopcock pressed in. The apparatus is left for a few minutes to make sure that no further change takes place.

The burettes are then half emptied by opening the stopcock *f*, and the vessel *A* lifted out of the water and tilted so that the solution of ammonium salt flows very slowly into the hypobromite. When the bulk of the ammonium sulphate has been decomposed, the bottle is shaken so that the hypobromite enters the tube *a*. When the evolution of gas has ceased—*i.e.*, when no further displacement of the water in the burette is observed—the bottle is replaced in the cooling trough and the apparatus allowed to stand for fifteen minutes. The water is then brought to the same level in both limbs and the volume of gas in *d* noted.

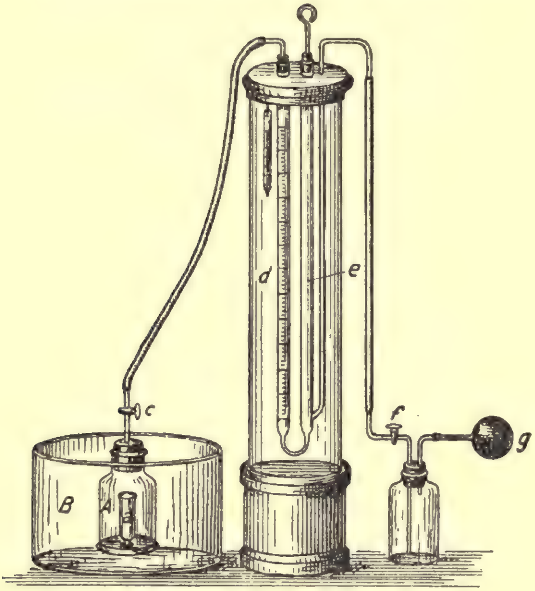


FIG. 29.

The hypobromite solution is prepared by dissolving 100 grs. of caustic soda in 250 c.c. of water and adding slowly from a burette, with cooling, 8 c.c. (=25 grs.) of bromine.

To eliminate any error which might arise from the absorption of nitrogen by the bromine solution, or from the incomplete decomposition of the ammonium salt, a blank experiment is made with a solution containing 20 grs. of pure dried ammonium sulphate per litre, 10 c.c. of this solution being decomposed with 50 c.c. of the bromine solution; 20 grs. of the sample are then dissolved in 1 litre of water, and 10 c.c. of this solution treated with 50 c.c. of the bromine solution exactly as before. In order to secure as far as possible similar conditions of temperature and pressure, no time should be lost between the experiments. The uncorrected volumes of gas obtained in the two experiments are directly proportional to the amounts of nitrogen present.

Example: The standard solution yields a c.c., the sample under investigation b c.c., of gas. Since pure ammonium sulphate contains 21·2 per cent. of nitrogen, the amount of nitrogen in the sample will be $=\frac{21\cdot 2 \times b}{a}$ per cent.

When a cold aqueous solution of caustic soda is saturated with bromine, sodium hypobromite is formed, according to the equation

$$Br_2 + 2NaOH = NaBrO + NaBr + H_2O.$$

The solution should be prepared immediately before use, as it does not keep well. Ammonia is oxidized quantitatively to nitrogen by sodium hypobromite and hypochlorite:

$$3NaBrO + 2NH_3 = 3NaBr + 3H_2O + N_2.$$

3. Determination of Free Sulphuric Acid.—50 c.c. of the solution prepared for the determination of ammonia are titrated with $\frac{1}{5}$ normal caustic soda, using methyl orange as indicator.

4. Determination of Residue after Ignition.—2 grs. of the substance are volatilized carefully in a tared platinum crucible partly covered with the lid. After cooling, the weight of the residue is ascertained.

II. Quicklime.

1. Determination of Free CaO.—50 grs. of a good average sample are weighed out rapidly on a superior hand-balance (sensitive to 0·1 gr.), cautiously slaked with water and washed into a litre flask. The mixture is cooled and diluted to the mark. After shaking well, 20 c.c. are removed by means of a pipette and titrated slowly with normal hydrochloric acid with constant stirring until the colour of the phenolphthaleïn indicator is discharged.

When phenolphthaleïn is used as indicator in the titration of a mixture of hydroxide and carbonate of an alkaline earth, the colour is discharged when the hydroxide is just neutralized.

The carbonate is not affected provided the above-mentioned precautions are observed—viz., the slow addition of the acid and vigorous stirring during the titration. (Compare Black Ash, determination 2, p. 100.)

2. Determination of $CaCO_3$.—50 c.c. of the suspension prepared for the determination of free lime are mixed with an excess of normal hydrochloric acid and heated gently until the carbonate is completely dissolved. After cooling, the solution is titrated back with normal caustic soda. From the amount of acid consumed deduct the volume corresponding to the free lime, and calculate the remainder into equivalent $CaCO_3$.

B.—Control of the Process.

Carbonators.

1. Determination of Total Ammonia.—The apparatus sketched in Fig. 26 (p. 90) is employed; 10 c.c. of the liquor are placed in the Erlenmeyer flask and distilled with excess of caustic soda solution. The ammonia is absorbed in normal sulphuric acid and the excess of acid titrated with normal sodium hydroxide, using methyl orange as indicator.

2. Determination of Free and "Carbonic" Ammonia.—(*a*) 10 c.c. of the liquor are titrated with normal sulphuric acid; this gives the amount of free ammonia *plus* "semi-combined" ammonia—*i.e.*, ammonia combined with carbonic acid. The free ammonia is then separated from the semi-combined as follows:

(*b*) 10 c.c. of the liquor are run into a 200 c.c. graduated flask, mixed with a measured volume of ammonia of known concentration and excess of barium chloride solution. The mixture is then diluted with distilled water to the mark. After passing through a dry filter, 100 c.c. of the solution are titrated with normal hydrochloric acid. Any ammonia *in excess* of the amount added represents the free ammonia originally present in the sample. An amount of acid equivalent to this excess of ammonia is deducted from the amount of acid consumed in titration (*a*) and the difference corresponds to the normal ammonium carbonate, $(NH_4)_2CO_3$, present. If the ammonia found in titration (*b*) is exactly *equal to* the amount added, the liquor does not contain any free ammonia and the whole of the sulphuric acid used in (*a*) corresponds to $(NH_4)_2CO_3$. Finally, if the ammonia found in titration (*b*) is *less than* the amount added, the carbonation of the liquor has resulted in the formation of ammonium bicarbonate (NH_4HCO_3). In this case the deficit of ammonia is expressed in terms of ammonium bicarbonate (1 mol. NH_3=1 mol. NH_4HCO_3) and an equivalent amount of acid is deducted from that used in the direct titration (*a*); the remainder corresponds, as before, to normal carbonate.

If the liquor contains free ammonia, only the normal carbonate can be present in addition, since bicarbonate and ammonia would neutralize each other. Before the ammonia is titrated, the carbonate must be precipitated by the addition of barium chloride:

$$BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl.$$

For the determination of carbonate in presence of bicarbonate, an excess of ammonia is added to convert the bicarbonate into normal carbonate—

$$NH_4HCO_3 + NH_4OH = (NH_4)_2CO_3 + H_2O.$$

The carbonate is then precipitated, as before, with barium chloride. After filtering, the residual ammonia in the filtrate is determined by titration, and the amount of bicarbonate calculated from the ammonia consumed.

Since it is impossible to know in advance whether the liquor contains free ammonia, or whether the carbonation has proceeded to a more advanced stage (an alkaline reaction or a smell of ammonia is no criterion, since neutral ammonium carbonate, owing to hydrolysis, also gives these indications), standard ammonia should always be added before the barium chloride, as a precaution against error.

If barium chloride were added to a solution containing ammonium carbonate or bicarbonate, without free ammonia, the bicarbonate would not be precipitated, since barium bicarbonate is soluble; the latter would thus take part in the titration and appear erroneously in the result as free ammonia.

The ammonia added should contain no trace of carbonate.

Pure ammonium hydroxide is prepared by distilling a saturated solution of ammonia with milk of lime and collecting the gas in freshly distilled water.

3. Determination of Combined Ammonia.—From the volume of normal sulphuric acid neutralized in the determination of total ammonia (1) is deducted the amount required for the titration of free and semi-combined ammonia (2, *a*). The remainder corresponds to combined ammonia, and is calculated to equivalent NH_4Cl.

The chemical reactions involved in the ammonia-soda process are the following:

When saturated solutions of sodium chloride and ammonium bicarbonate are mixed together, or, similarly, when a mixture of gaseous ammonia and carbon dioxide is passed into saturated sodium chloride solution, sodium bicarbonate (which is almost insoluble) is precipitated:

$$NaCl + NH_4HCO_3 = NH_4Cl + NaHCO_3.$$

Since bicarbonate can readily be converted into neutral carbonate,

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O,$$

these equations suggest a method of preparing sodium carbonate from common salt, which at first sight would appear to be comparatively simple.

In practice, however, great difficulties were experienced in working out the mechanical details of the plant. Eventually E. Solvay succeeded in constructing a practicable apparatus, and to him is due the credit of having established the process on a commercial basis and demonstrated its superiority over the older Leblanc process.

The ammonia-soda plant is generally erected in the vicinity of rock-salt deposits, where water can be introduced and the brine pumped out through bore-holes sunk on the spot, as, for instance, at Fleetwood in Lancashire. At some works—*e.g.*, at Duisburg in Westphalia and Kalk near Cologne—the liquor is prepared by dissolving solid rock salt imported from a distance; at others, notably in the Cheshire brine districts, natural brine is used.

The saturated solution of sodium chloride must be freed from impurities such as salts of magnesia and iron, either before use by treatment with sodium carbonate or milk of lime, or subsequently during the process itself (*vide infra*).

Gaseous ammonia is then passed into the concentrated brine, the amount being so calculated that for every molecule of sodium chloride 1 molecule of ammonia is added. This operation takes place in closed wrought-iron cylinders (absorbers), in which the ascending current of gas meets the downflowing brine. The absorbers are cooled internally with water. If the brine has not been purified beforehand, any iron, lime, or magnesia present is here precipitated by the carbon dioxide, a certain amount of which is always passed in with the ammonia. The liquor is then clarified in a settling tank and the clear ammoniacal brine conveyed to the carbonating apparatus, where it is treated with carbon dioxide. The carbonating plant consists of a tower 15 to 20 metres in height and 1½ to 2 metres in diameter, in which are arranged a number of slightly arched perforated plates extending almost completely across it at intervals of about 1 metre; these divide the ascending stream of carbon dioxide into small bubbles, thus bringing it into intimate contact with the ammoniacal liquor. In place of a single high tower, five or six smaller towers arranged in series are sometimes employed.

The bulk of the carbon dioxide used is prepared by burning limestone, but an auxiliary supply is obtained from the calcination of the sodium bicarbonate produced in the process. The gases are forced through the tower at a pressure of 2½ atmospheres to overcome the high resistance of the column of liquid. During the process of carbonation the liquor must be kept cool. The most suitable temperature is 30° C., since this favours the separation of the bicarbonate in the form of coarse crystals, which can be readily filtered. Towards the end of the operation the liquor is cooled still further to secure a more complete separation of the sodium bicarbonate.

When the precipitation is complete, the magma is run from the carbonating tower into centrifugal machines or filter-presses, where the bicarbonate is separated. The latter is washed with a saturated solution of pure sodium bicarbonate to remove any mother-liquor and then calcined in Thélen pans at 250° C., at which temperature it is readily converted into the normal carbonate, with loss of carbon dioxide.

One of the most important operations in the whole process is the recovery of the ammonia from the mother-liquor obtained after filtration and from the wash-water used. The liquor is treated in high towers, first with steam and then with lime from the carbonic acid generators, which is added in large unslaked lumps, so that the heat of hydration is utilized.

The ammonia liberated according to the equation

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$$

is used over again.

In a well-managed plant the loss of ammonia in the cycle of operations should not exceed 2 to 3 per cent. The loss is made good by the addition of ammonium sulphate or concentrated ammonium hydroxide.

In this process large quantities of calcium chloride are obtained as a by-product. Up to the present time no economical method has been devised for the recovery of chlorine from this residue, which is run to waste.

12. WELDON MUD.

1. Determination of Manganese Dioxide.—The manganese mud is shaken vigorously in a bottle, and 10 c.c. removed by means of a special pipette having a very wide delivery tube. After wiping the stem with a piece of moist filter-paper, the sample is run into an Erlenmeyer flask and the sediment washed out of the pipette with a jet of distilled water; 50 c.c. of a $\frac{1}{4}$ normal *acid* solution of ferrous sulphate (prepared by dissolving equal parts by weight of crystalline ferrous sulphate and concentrated sulphuric acid) are then added, the flask rocked gently until the paste is completely dissolved, and the excess of ferrous sulphate titrated back with potassium permanganate. The result is expressed in grams of MnO_2 in 1 litre of mud.

By the addition of ferrous sulphate, not only the manganese dioxide, but also the lower oxides present—viz., Mn_2O_3 and Mn_3O_4 (which, as explained below, may be regarded as compounds of divalent and tetravalent manganese)—are reduced to the divalent condition.

2. Determination of Total Manganese. — 100 c.c. of the mud are delivered into an Erlenmeyer flask as in (1), and heated with concentrated hydrochloric acid until the evolution of chlorine has ceased. The solution is then neutralized with precipitated calcium carbonate or caustic soda, a concentrated solution of bleaching powder (previously filtered) is added and the mixture heated until a faint red coloration is produced. The colour is discharged by adding alcohol drop by drop, after which the precipitate of manganese dioxide is filtered off and washed until the washings give no reaction with starch-potassium iodide paper. The precipitate, with the filter, is transferred to an Erlenmeyer flask and digested with a measured quantity of acid ferrous sulphate (prepared as above) sufficient to dissolve it completely.

The excess of ferrous sulphate is then titrated back with permanganate. The result is calculated in terms of MnO_2 per litre of mud.

In order that the whole of the manganese may be converted into dioxide, it is necessary first to decompose the lower oxides, Mn_2O_3 and Mn_3O_4. These are completely reduced to the divalent condition by boiling with hydrochloric acid. On heating the neutralized solution with bleaching powder, they are oxidized to the tetravalent condition. On continued heating with excess of this reagent, the oxidation proceeds still further and traces of permanganate are formed, which must be reduced back to the tetravalent condition by the addition of alcohol.

3. Determination of the "Base."—10 c.c. of the mud are pipetted into a 200-c.c. flask, mixed with 25 to 50 c.c. of normal oxalic acid, diluted with water to about 100 c.c., and heated on a water-bath at 70° to 80° C. until the whole of the manganese dioxide is reduced and the precipitate is nearly white. The solution is cooled and made up to the mark, after which an additional 2 c.c. of distilled water is added to allow for the volume of the precipitate. The excess of oxalic acid is determined by titrating 100 c.c.—passed through a *dry* filter—with normal caustic soda, using phenolphthaleïn as indicator.

By "base" is understood the ratio of the divalent monoxides (chiefly CaO and MnO, together with a small amount of MgO and FeO) to the manganese dioxide present. The importance of this determination lies in the fact that the dioxide alone takes part in the production of chlorine, the monoxide merely passing into solution.

In calculating the "base," note that the oxalic acid added to the neutral slime serves in the first place to reduce the manganese dioxide to manganous oxide, according to the equation

$$MnO_2+(COOH)_2=MnO+2CO_2+H_2O.$$

An equal amount of oxalic acid is then neutralized by the manganous oxide produced in this reaction.

The bases originally present, including MnO and CaO, also neutralize their equivalent amounts of oxalic acid. Since normal oxalic acid is used in this titration, the volume of

$\frac{1}{4}$ normal ferrous sulphate required in (1) should be calculated to normal solution.

Suppose that in the titration (1) a c.c. of *normal* ferrous sulphate are required, and in the titration (3) b c.c. of oxalic acid. Of the latter, a c.c. are used in the reduction and an equal quantity in neutralizing the manganous oxide, the remainder, $b-2a$ c.c., corresponding to the bases.

Hence the ratio of monoxides to manganese dioxide, or "base," is expressed by $\frac{b-2a}{a}$.

"Weldon mud" is the name given to the regenerated manganese liquor which serves for the production of chlorine in Weldon's process. The following is a brief outline of this process:

Pyrolusite is treated with concentrated hydrochloric acid in vats constructed of slabs of sandstone or granite tarred on the inside. At first the reaction takes place in the cold, part of the chlorine remaining in solution as manganese tetrachloride—

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$

Towards the end of the operation the solution is heated to about 90° C. by blowing in steam, whereupon the manganese tetrachloride is converted into manganous chloride, with evolution of chlorine—

$$MnCl_4 = MnCl_2 + Cl_2.$$

Owing to the high price of pyrolusite, the use of any large quantity of fresh material would be unprofitable; hence the manganous chloride liquor is submitted to a regenerative process and used over and over again in the stills. The liquor, which contains no free chlorine, but always a slight excess of hydrochloric acid, is run from the still into a vat ("neutralizing well") of similar construction, provided with a mechanical stirring apparatus, and is neutralized therein with finely ground lime (limestone or chalk), any iron present being precipitated as hydroxide. From here the turbid solution is pumped into a large settling tank of wrought iron. After complete clarification—which usually takes several hours—it is run into tall towers ("oxidizing towers"), where the actual regeneration takes place. The temperature is raised to 50° to 60° C. by blowing in steam, an excess of milk of lime is added and a rapid current of air from a compressor forced through the liquor, which gradually darkens in colour and finally becomes quite black.

While, on the one hand, tetravalent manganese in acid solution is easily reduced to the divalent condition by such reducing agents as ferrous sulphate, sulphurous acid, and hydrochloric acid, divalent manganese is very unstable in alkaline solution, readily passing into the trivalent condition on gentle oxidation, and into the tetravalent condition when more powerful oxidizing agents are employed.

When the manganous hydroxide, $Mn(OH)_2$, set free by treatment with strong bases, is oxidized with air, the oxidation does not proceed beyond the formation of a mixture of Mn_3O_4, with a small proportion of Mn_2O_3, even if the blowing be continued for a very long time. Weldon found, however, that in presence of a large excess of lime the conversion of divalent into tetravalent manganese takes place under this treatment almost quantitatively.

The reaction may be explained as follows: Manganous hydroxide, $Mn(OH)_2$, is a base and reacts with acids to form salts, such as $MnSO_4$ and $MnCl_2$. Tetravalent manganese, on the contrary, has a well-defined acid character. (The trivalent variety, which is formed on gentle oxidation, is not considered here.) Thus hydrated MnO_2 is acid to litmus, and displaces carbonic acid from salts, forming manganites. When air is blown into dibasic manganous hydroxide, $Mn(OH)_2$, part of the manganese is oxidized to acidic tetravalent manganese, and the two then combine to form salts which have divalent manganese in the base and tetravalent manganese in the acid radicle.

Calling the compounds H_2MnO_3 ($=MnO_2+H_2O$) *metamanganous acid*, and H_4MnO_4 ($=MnO_2+2H_2O$) *orthomanganous acid*, the oxide $MnMnO_3=Mn_2O_3$ may be regarded as the manganous salt of metamanganous acid, and the oxide $Mn_2MnO_4=Mn_3O_4$ as the manganous salt of the orthomanganous acid. The former contains 1 molecule of basic and 1 molecule of acidic manganese; the latter 2 molecules of basic and 1 molecule of acidic manganese. Since these two compounds alone are formed when manganous hydroxide is exposed to a current of air, it must be assumed that the free base $Mn(OH)_2$ and not the divalent manganese salts, can be oxidized by atmospheric oxygen. (The more powerful oxidizing agents, such as bleaching powder, chlorine or bromine, behave differently, converting the combined divalent manganese also into tetravalent manganese.)

The influence of excess of lime on the oxidation is thus easily understood. Lime, being a stronger base, prevents the formation of mangano-manganites by itself entering into combination as calcium manganite, so that the whole of the manganese base remains free and is thus completely oxidized to the tetravalent acid.

Continuing his investigations, Weldon discovered that the addition of excess of lime not only brings about more complete oxidation, but also greatly accelerates the reaction. Moreover, the presence of calcium chloride formed by the interaction of manganous chloride and calcium hydroxide,

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2,$$

promotes the reaction, probably owing to the fact that both lime and manganous hydroxide are slightly more soluble in calcium chloride solution than in water.

The minimum amount of lime to be added is carefully calculated, since any unnecessary excess would cause wastage of hydrochloric acid in the subsequent operation of generating chlorine. The addition of 1 molecule of lime to 2 molecules of manganese is sufficient. With this amount of lime an acid calcium metamanganite, $Ca(HMnO_3)_2$, is formed, so that for every 2 molecules of manganese taking part in the production of chlorine only 1 molecule of calcium requires to be neutralized. In an efficiently regenerated Weldon mud, 80 to 85 per cent. of the manganese present should exist in this form; the remainder usually consists of Mn_3O_4.

The regenerated material is run out of the oxidizing towers into settling tanks, where the mud is deposited. The clear solution of calcium chloride is drawn off and the mud returned to the chlorine still, which has been previously charged with hydrochloric acid. Weldon mud is much more easily decomposed than pyrolusite.

The history of the Weldon process resembles that of the Leblanc soda process. Just as the latter for a long period competed successfully with the ammonia-soda process, which, although superior in principle, had not been worked out sufficiently in detail, so the Weldon process—while undoubtedly inferior in principle to the Deacon process—maintained its lead for several decades, owing to the imperfect development of its rival. (In the Weldon process over 60 per cent. of the chlorine in the hydrochloric acid used is lost as calcium chloride; in the Deacon process the whole of the hydrochloric acid is theoretically convertible into chlorine.)

The Weldon process is now falling into disuse; it is only employed in localities where large supplies of very cheap hydrochloric acid are available.

13. STASSFURT POTASH SALTS.

A.—Crude Salts.

1. Determination of Potash—(*a*) "*Platinum Chloride*" *Method.*—10 grs. of the finely ground salt are boiled for fifteen minutes with 200 c.c. of water in a 500 c.c. graduated flask. After cooling, the solution is made up to the mark with water and passed through a *dry* filter; 50 c.c. of the filtrate, transferred to a 200 c.c. flask, are acidified slightly with hydrochloric acid, heated to boiling and the sulphate precipitated by adding barium chloride drop by drop, taking care to avoid excess of the reagent. After allowing to cool, the flask is filled to the mark with water and the suspension is filtered. A portion of the filtrate—50 c.c. if the salt contains less than 20 per cent. of potash, 25 c.c. if the potash exceeds this amount—is evaporated to dryness in a porcelain dish on the water-bath. The residue is dissolved in 5 c.c. of hot water and a very slight excess of chloroplatinic acid added, together with 50 c.c. of 96 per cent. alcohol. The mixture is well stirred and set aside for one hour in a dark place protected from ammonia fumes; on hot days it should also be cooled. The precipitate of potassium chloroplatinate is then filtered through a tared Gooch crucible, previously dried at 120° C., washed with a small quantity of 96 per cent. alcohol, dried at 120° for thirty minutes, cooled and weighed.

Potassium is separated from sodium by treating the mixed chlorides with sufficient chloroplatinic acid to convert both completely into the corresponding chloroplatinates, K_2PtCl_6 and Na_2PtCl_6. The sodium salt is easily soluble in alcohol, while that of potassium is practically insoluble. If too little chloroplatinic acid be added, part of the sodium is precipitated with the potassium as chloride on the addition of alcohol. The sulphates must first be converted into chlorides, otherwise a certain amount of sodium sulphate—which is practically insoluble in alcohol—

may be precipitated, even in presence of excess of chloroplatinic acid.

By this abbreviated method—adapted from that of Fresenius—potassium can also be separated from the alkaline earths and magnesium, since the latter, like sodium, forms chloroplatinates, which are soluble in alcohol. For this reason, also, the removal of any slight excess of barium chloride used in the precipitation is unnecessary. This reagent should, however, be added with the greatest care, otherwise the precipitate may be contaminated with barium salts, notwithstanding the fact that barium chloroplatinate is soluble in alcohol.

(*b*) *Perchloric Acid Method.*—10 grs. of the sample are dissolved and treated exactly as in (*a*), as far as the precipitation with barium chloride. In this case a slight excess of the reagent is of no consequence. After cooling, the solution is diluted to the mark with water and filtered; 50 c.c. of the filtrate are pipetted into a glazed porcelain (or glass) dish and mixed with a quantity of perchloric acid about 50 per cent. in excess of that required for the complete decomposition of the salts. The mixture is then heated on a water-bath until it ceases to smell of hydrochloric acid and heavy white fumes of perchloric acid are evolved. After allowing to cool, the residue is covered with about 20 c.c. of 96 per cent. alcohol and broken up with a glass rod. It is then rinsed into a weighed Gooch crucible previously dried at 120° C., where it is washed, first with alcohol containing 0·2 per cent. of perchloric acid and then with a small quantity of pure absolute alcohol, to remove the last trace of perchloric acid, after which it is dried at 120° C. for half an hour.

This method, like the preceding, can be used for the separation of potassium from sodium, magnesium, and the alkaline earths, since the perchlorates of these metals, with the exception of potassium, are readily soluble in alcohol. In point of accuracy it is not inferior to the platinum method, and it may be employed with advantage in the analysis of salts containing sulphates, since the result is not affected by the presence of excess of barium chloride.

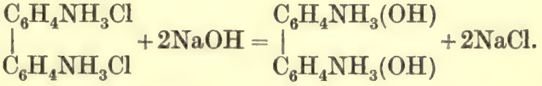
The concentration of the aqueous perchloric acid provided in the laboratory may be determined either by finding its specific gravity (see Table, p. 227) or by titration with caustic soda; in the latter case any indicator may be used, since perchloric acid possesses *strongly* acid properties.

2. Determination of Sulphuric Acid (W. Müller's Benzidine Method).—10 to 50 c.c. (according to the amount of sulphate present) of the solution prepared for the determination of potassium are carefully neutralized (if necessary), transferred to a 200 c.c. flask, diluted with a small quantity of water, and heated to about 80° C. on a water-bath. A measured excess of a solution of approximately 3 per cent. benzidine chloride is then slowly added, the flask being gently shaken. After standing on the water-bath for a few minutes, the flask is removed and cooled quickly. It is then filled to the mark with water. An aliquot portion of the solution is passed through a *dry* filter and the excess of benzidine chloride titrated with pure caustic soda, using phenolphthaleïn as indicator. The titre of the benzidine solution is similarly determined with caustic soda.

It is well known that very feeble bases do not react with the weak acid phenolphthaleïn. Hence, in presence of this indicator the acids combined in the salts of such bases—provided they are strong acids—can be titrated with alkalis as if they were free. The salts of aluminium furnish a good example. When aluminium chloride is titrated with caustic soda according to the equation

$$AlCl_3 + 3NaOH = Al(OH)_3 + 3NaCl,$$

the red colour of the phenolphthaleïn appears only after the chloride has been completely neutralized. The titration of the salts of benzidine, a weak organic base, is analogous; thus,



$$\begin{array}{l}C_6H_4NH_3Cl\\ |\\ C_6H_4NH_3Cl\end{array} + 2NaOH = \begin{array}{l}C_6H_4NH_3(OH)\\ |\\ C_6H_4NH_3(OH)\end{array} + 2NaCl.$$

When benzidine chloride is added to a solution of potassium salts containing sulphate, the sulphuric acid is precipitated quantitatively as insoluble benzidine sulphate. From the amount of benzidine chloride consumed, as determined by titration, the equivalent of sulphuric acid originally present in the sample is calculated.

B.—Refined Salts.

3. Determination of Sodium Chloride in High-Grade Potassium Chloride (Böttger and Precht's Method).—10 grs. of the sample of potassium chloride are heated gently in a 200 c.c. flask with 20 c.c. of a 0·5 per cent. solution of potassium carbonate until completely dissolved. The hot solution is diluted to the mark with absolute alcohol and the flask shaken vigorously for a few minutes to ensure thorough mixing. After cooling completely, the solution is made up to 205 c.c. with alcohol and passed through a *dry* filter; 100 c.c. of the filtrate are treated with a little hydrochloric acid to decompose the potassium carbonate, and then evaporated to dryness in a weighed porcelain dish. The residue, consisting of a mixture of sodium and potassium chlorides, is ignited gently and weighed. The sodium is then estimated indirectly, either by converting the mixed chlorides into sulphates (evaporating with sulphuric acid) or by separately determining the potassium by precipitation with chloroplatinic or perchloric acid and hence calculating the amount of sodium chloride.

This method should be used only in the case of potassium chloride containing 95 to 99 per cent. KCl.

By the addition of alcohol to the concentrated solution of the salt, the major portion of the potassium chloride is precipitated, while the whole of the small amount of sodium present remains in solution. By means of this neat process of concentration the estimation of sodium, which can only be made indirectly, is accomplished with much greater certainty. The object of adding potassium carbonate is to precipitate any magnesium or calcium present.

In converting the chlorides to sulphates, the residue, after the excess of sulphuric acid has been volatilized, is heated for a few minutes to dull redness only, with the addition of a little solid ammonium carbonate. In this way the pyrosulphates, which are formed from the bisulphates during the preliminary treatment and only give up SO_3 quantitatively when *strongly* ignited, are converted into neutral sulphates, and the volatile ammonium sulphate is expelled:

$$K_2S_2O_7 + (NH_4)_2CO_3 = K_2SO_4 + (NH_4)_2SO_4 + CO_2.$$

The amount of sodium chloride present is calculated indirectly in the following way:

If the weight of the mixed chlorides be a grs., that of the mixed sulphates b grs., and if x grs. be the weight of KCl in the mixed chlorides, then the weight of NaCl is $(a-x)$ grs.

On converting into sulphate, the weight of the potassium salt increases in the ratio $2KCl : K_2SO_4$, that of the sodium salt in the ratio $2NaCl : Na_2SO_4$; hence

$$b = \frac{K_2SO_4}{2KCl}x + \frac{Na_2SO_4}{2NaCl}(a-x),$$

which reduces to $x = 26{\cdot}21a - 21{\cdot}57b$ and $(a-x) = 21{\cdot}57b - 25{\cdot}21a$.

All calculations of indirect analyses are made similarly.

Instead of converting the chlorides into sulphates, the sodium can be determined indirectly by titrating the mixed chlorides with decinormal silver nitrate. In this case, if a grs. of the mixed chlorides contain c grs. of chlorine, the equation takes the form

$$c = \frac{Cl}{KCl}x + \frac{Cl}{NaCl}(a-x).$$

Immense deposits of potash salts occur in Germany, where the supplies in the vicinity of Stassfurt, Aschersleben and Hildesheim almost suffice to meet the demand of the entire world. The formation of these deposits is supposed to have been due to the gradual desiccation of a large land-locked sea which covered the North German Plain. By counting the laminations in certain thin seams of anhydrite ($CaSO_4$) which are found interstratified with layers of rock salt, it is estimated that the process of deposition extended over a period of about 10,000 years. Van't Hoff, who, after many years of research, explained the mode of formation of these salt deposits, has shown by means of his "Geological Thermometer" that a temperature of over 70° C. must have prevailed when the various salts were formed.

The most important potassium salts which occur in the Stassfurt deposits are:

Carnallite, $KCl.MgCl_2.6H_2O$.
Kainite, $KCl.MgSO_4.3H_2O$.
Crude sylvine,* a mixture of KCl and NaCl.
Schoenite, $K_2SO_4.MgSO_4.6H_2O$.
Polyhalite, $K_2SO_4.MgSO_4.2CaSO_4.2H_2O$.

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* Not to be confused with sylvinite, which is the name given to crude kainite or hartsalz when the percentage of potash exceeds 13 per cent. K_2O. Sylvine proper has the formula KCl; the percentage of KCl in crude sylvine varies from 25 per cent. to 90 per cent.—*Tr.*

The individual salts, however, are never obtained in a pure condition, but invariably contain a considerable admixture of sodium chloride. Usually they also contain some *anhydrite*, $CaSO_4$, occasionally *boracite*, $6MgO.8B_2O_3.MgCl_2$ (which is extracted for the preparation of boric acid), and iron chloride, which crystallizes with carnallite as *Douglasite*—a mixture having the approximate composition $KCl.FeCl_2.6H_2O$. The last named reacts with water according to the equation.

$$6FeCl_2 + 6H_2O = 4FeCl_3 + 2Fe(OH)_3 + 3H_2,$$

and frequently the hydrogen evolved accumulates in the salt-mines, forming an explosive mixture. Carnallite generally contains also a small amount of bromine, which is recovered from the end-liquors.

"*Hartsalz,*" a mixture of crude sylvine ($KCl + NaCl$) with *kieserite*, $MgSO_4.H_2O$, is also widely distributed.

At Stassfurt the potash salts are won by mining. The hard mass is broken down by blasting, an adequate number of supporting pillars being left to prevent the collapse of the workings. The crude salts are hauled to the surface, crushed, and marketed chiefly in the raw state. A small portion is worked up for the production of potassium chloride and sulphate, and of potassium magnesium sulphate, certain by-products being recovered at the same time (*vide infra*). About 80 per cent. of the potash salts extracted, including the whole of the raw salts as well as a considerable part of the purified material, are consumed in agriculture. The richest potash fertilizers, such as high-grade sylvine, hartsalz and kainite, containing up to 42 per cent. K_2O, are chiefly exported, while the inferior salts, containing from 12 to 15 per cent. K_2O, which cannot be profitably shipped, are used locally.

The most important of the potassium salts utilized in the chemical industry is the chloride, large quantities of which are used in the manufacture of caustic potash and potassium carbonate, and to a less extent for the preparation of potassium nitrate, chlorate, chromate and other salts. The raw material employed is chiefly carnallite, with some sylvine and hartsalz. The crude carnallite is broken up in jaw-crushers or crushing rolls and conveyed by means of elevators into tall cast-iron tanks, where it is treated with a concentrated liquor containing magnesium chloride and sodium chlorides (obtained from a later process) previously heated to boiling. The temperature is maintained for some time by blowing in steam. Only the carnallite is readily soluble in this hot liquor, while the kieserite and much of the sodium chloride present remain in the residue with the anhydrite, clay and sand. The liquor is discharged into clarifying tanks, where the solid matter settles out, and the clear extract is run while still hot into iron crystallizing pans, where it is left standing for two or three days. The crystalline product so obtained, consisting of a mixture of potassium and sodium chlorides, is shovelled into a vat having a perforated false bottom, where it is washed with water and raised to a concentration of 80 to 90 per cent. KCl (" KCl I., low grade "). The mother-liquor from this is evaporated until it contains about 30 per cent. of magnesium chloride, whereupon a large amount of sodium chloride, called " bottom salt," separates out. The concentrated liquor is then allowed to cool and yields a crop of pure carnallite. This is dissolved in the smallest possible quantity of boiling washings from KCl I. and on cooling yields a rich potassium chloride, which is concentrated to 98 to 99 per cent. KCl by washing with water (KCl II., " high-grade potassium chloride ").

The washings from KCl II., together with part of the mother-liquor, are concentrated by evaporation, and again used in the cycle of operations to dissolve the crude material. The end-liquors contain 0·2 to 0·3 per cent. of bromine, derived from *brom-carnallite,* $KBr.MgBr_2.6H_2O$, originally present in the carnallite, with which it is isomorphous.

The bromine is recovered either by saturating with gaseous chlorine, by adding the calculated amount of liquid chlorine, or by electrolysis. In the last case the bromine is liberated either directly or indirectly by the action of the chlorine primarily set free. The bromine is then distilled off and condensed in an earthenware cooling worm. Finally, a small portion of the debrominated mother-liquor is evaporated and used for the preparation of magnesia and of hydrochloric acid; the major portion, however, is run to waste.

From the kieserite and rock salt in the residue remaining after the preliminary extraction, Epsom salt and Glauber's salt may be obtained.

For the preparation of *Epsom salt,* $MgSO_4.7H_2O$, the residue is freed from sodium chloride by washing with cold water, in which the kieserite is almost insoluble. The kieserite is then dissolved in hot water, from which, on cooling, it crystallizes in the form of Epsom salt.

Glauber's salt, $NaSO_4.10H_2O$, is formed from sodium chloride and magnesium sulphate at a low temperature (– 5° C.) according to the equation

$$2NaCl + MgSO_4 + aq. = Na_2SO_4.10H_2O + MgCl_2 + aq.$$

In the cold season it is also prepared from carnallite residues.

Potassium magnesium sulphate and potassium sulphate are prepared from kainite, or hartsalz rich in potash. When these salts are dissolved in hot water, potassium magnesium sulphate separates out on cooling, thus:

$$2KCl + 2MgSO_4 + aq. = K_2SO_4.MgSO_4.6H_2O + MgCl_2 + aq.,$$

which after calcining and grinding is used as a fertilizer. From this double salt pure potassium sulphate can be obtained by adding to a hot concentrated solution, with constant stirring, an excess of solid potassium chloride,

$$K_2SO_4.MgSO_4 + 2KCl = 2K_2SO_4 + MgCl_2.$$

The mother-liquor, which still contains potassium chloride, is evaporated and used again.

14. SUPERPHOSPHATE.

1. Determination of Water-Soluble Phosphoric Acid.—10 grs. of the superphosphate, contained in a stout 500 c.c. graduated flask, are mixed with 400 c.c. of water and shaken vigorously for thirty minutes, either by hand or in a mechanical shaking apparatus. The flask is then filled to the mark with water; 50 c.c. of the filtered extract are mixed with an equal volume of ammoniacal citrate solution (prepared as described below) and 25 c.c. of magnesia mixture (see below), after which the liquid is stirred for thirty minutes. For this purpose a mechanical stirrer is employed, consisting of a strip of glass or vulcanized rubber 2 to 3 cm. in width, or of a glass rod bent in the form of a zigzag, driven by means of a small water turbine or electric motor. The precipitate can then be filtered off immediately. After washing with a 2 per cent. solution of ammonia until the washings no longer produce a cloudiness when tested with silver nitrate, the precipitate is burnt moist in a platinum crucible, ignited and weighed.

Preparation of Reagents.—(1) Ammoniacal citrate solution is prepared by dissolving 50 grs. of citric acid in 250 c.c. of 20 per cent. ammonia. (2) Magnesia mixture is made by dissolving 11 grs. of chemically pure crystalline magnesium chloride and 14 grs. of ammonium chloride in 130 c.c. of water and adding 70 c.c. of 8 per cent. ammonia. Should any of the substance remain undissolved, or a precipitate appear after long standing, the solution must be filtered.

2. Determination of Total Phosphoric Acid.—5 grs. of the sample are boiled with 50 c.c. of aqua regia in a 250 c.c. flask for half an hour. After cooling, the solution is diluted to the mark and filtered; 50 c.c. of the filtrate are mixed with 50 c.c. of ammoniacal citrate solution and 25 c.c. of magnesia mixture, and treated as in (1).

The direct precipitation of phosphoric acid with magnesia in presence of the bases contained in the superphosphate—viz., lime, alumina and iron oxide—is rendered possible by the previous addition of citric acid, $(CH_2)_2.COH.(COOH)_3$, with which these bases combine (as they do with other organic substances containing an hydroxyl group, *e.g.*, tartaric acid and sugar) to form complex compounds. The latter neither give a precipitate with ammonia nor separate as phosphate when the solution is made alkaline.

In agricultural laboratories the above method has almost completely superseded the older and more tedious method of separation in which the phosphoric acid is first precipitated with ammonium molybdate (as ammonium phosphomolybdate), and then, after dissolving this in ammonia, reprecipitated with magnesia mixture.

The precipitation of magnesium ammonium phosphate is accelerated to such an extent by agitation that the filtration can be made after stirring for half an hour instead of after several hours in the usual way.

Of the mineral substances required for the nutrition of plants, the soil usually contains in combination sufficient lime, magnesia, iron oxide, sodium, chlorine, sulphuric and silicic acids; but the principal plant foods—viz., phosphoric acid, potassium and nitrogen compounds, which are removed in large quantities when the crops are harvested—soon become exhausted and require frequent replenishing. From the earliest times this has been done by manuring with stable dung. At the present day, however, the supply of natural manure is often inadequate, and the deficiency is made up by using artificial fertilizers. Potash and nitrogen are available in the form of the Stassfurt salts (p. 119) and Chile saltpetre (p. 90), phosphorus in a variety of products of animal or vegetable origin. The bone-substance of animals consists mainly (about 80 per cent.) of normal tricalcium orthophosphate, $Ca_3(PO_4)_2$. Large deposits of fossil bones or *osteolites* and enormous quantities of *coprolites*, the petrified excrement of prehistoric animals (especially the Saurians of the Jurassic period) are found in England and Germany. Of animal origin also are the recent and partly mineralized *guano phosphates* formed from the excreta of birds of the present and former ages, which have accumulated to an enormous thickness in certain localities, notably on the coasts and islands of Central and South America (especially Peru), and in Africa.

The *mineral phosphates* are of even greater importance.

Extensive deposits of phosphates, phosphorites, and apatites, $3Ca_3(PO_4)_2.(CaCl_2,Fl_2)$, occur in Spain (Estremadura), the United States (South Carolina, Florida and Tennessee), in Canada and in Africa (Algeria); also in France (Somme phosphate), Norway and Belgium.

The phosphorus contained in bones and mineral—or mineralized phosphates—exists in the form of tricalcium phosphate, which is practically insoluble, and hence is but slowly assimilated by plants; for fertilizing it has first to be made available by conversion into an easily soluble form.

The calcium salts of orthophosphoric acid are:

(1) Tricalcium phosphate, $Ca_3(PO_4)_2$, insoluble in water and in weak organic acids.

(2) Dicalcium phosphate, $CaHPO_4$, insoluble in water, soluble in weak organic acids. This is called " citrate-soluble," since it dissolves readily in dilute citric acid.

(3) Monocalcium phosphate, $Ca(H_2PO_4)_2$, readily soluble in water.

The roots of plants, owing to their slightly acidic action, are capable of assimilating dicalcium phosphate, but in the preparation of artificial fertilizers the aim is to convert the phosphorus as far as possible into the water-soluble monocalcium salt, in which form it permeates the soil more uniformly.

For this purpose the phosphatic material is treated with sulphuric acid. Crude phosphate rock is first pulverized in crushing rolls or ball mills. Bones are submitted to a preliminary treatment with benzene for the removal of fats, or are calcined to bone ash. The powdered material is then brought into a cast-iron vat provided with a stirrer, where it is well mixed with sulphuric acid and then immediately discharged into large chambers ("dens") beneath, where it remains for several hours, until the process of decomposition is complete and the mass thickens and "sets." The chambers are then uncovered, and well ventilated to facilitate the escape of the gaseous hydrofluoric acid and silicon fluoride (SiF_4) which are liberated from the fluorine compounds present in the raw material.

The amount of sulphuric acid added is so calculated that for every molecule of tricalcium phosphate 2 molecules of acid are used, *plus* a further small quantity sufficient to convert the bases present (iron oxide and alumina) into neutral sulphates. The precise amount is generally determined by experiment. The process of decomposition takes place in two stages. By the first reaction in the vat two-thirds of the tricalcium phosphate is decomposed, with the formation of free phosphoric acid,

$$3Ca_3(PO_4)_2 + 6H_2SO_4 = 4H_3PO_4 + Ca_3(PO_4)_2 + 6CaSO_4 \ldots\ldots\ldots (1).$$

During the hardening of the mass in the cellars, a secondary reaction takes place between the free phosphoric acid and the still undecomposed tricalcium phosphate, according to the equation

$$4H_3PO_4 + Ca_3(PO_4)_2 = 3Ca(H_2PO_4)_2 \ldots\ldots\ldots (2).$$

The concentration of the acid employed is such that the amount of water just suffices for the crystallization of the monocalcium phosphate and gypsum, so that a dry mixture having the composition $Ca(H_2PO_4)_2.H_2O + 2CaSO_4.2H_2O$ is produced. This mixture—which also contains varying quantities of silica and sulphates of iron and aluminium, according to the quality of the raw phosphate employed—is called "superphosphate." The mass is crushed, and is then ready for distribution.

The price of superphosphate depends upon its content of water-soluble phosphate, which is determined by the method given above. The determination of the total phosphoric acid is only made for the purpose of controlling the process.

Superphosphate deteriorates on long standing, the percentage of water-soluble phosphoric acid gradually diminishing. This change is called "reversion." It may result from the use of an insufficient quantity of sulphuric acid, the undecomposed tricalcium phosphate subsequently reacting slowly with the monocalcium phosphate to form insoluble dicalcium phosphate, thus:

$$Ca(H_2PO_4)_2.H_2O + Ca_3(PO_4)_2 + 7H_2O = 4CaHPO_4.2H_2O.$$

Reversion, however, is mainly due to the presence of iron compounds in the crude phosphate. On treatment with acid, these are converted into ferric sulphate, which readily reacts with monocalcium phosphate, forming insoluble ferric phosphate and free sulphuric acid,

$$Fe_2(SO_4)_3 + Ca(H_2PO_4)_2 = 2FePO_4 + CaSO_4 + 2H_2SO_4.$$

For this reason phosphates containing more than 2 per cent. of iron are seldom employed for the manufacture of superphosphates.

Superphosphates containing alumina and silica also show a tendency to revert, possibly owing to reactions such as the following:

$$Al_2(SiO_3)_3 + 2Ca(H_2PO_4)_2 = 2CaHPO_4 + 2AlPO_4 + 3H_2SiO_3.$$

15. BASIC SLAG (THOMAS PHOSPHATE).

1. Determination of Total Phosphoric Acid.—5 grs. of the sample, contained in a 250 c.c. flask, are moistened with a little water, mixed with 25 c.c. of concentrated sulphuric acid, and heated strongly over a wire gauze for about fifteen minutes to a temperature at which white fumes are evolved. During the heating the flask should be shaken frequently to prevent the formation of a crust. After cooling, the solution is diluted to the mark with water and filtered; 50 c.c. of the filtrate are treated by the citrate method as described under Superphosphate (p. 127).

The silica present in basic slag is unaffected by sulphuric acid; hence the advantage of using this in preference to aqua regia for the decomposition (*vide infra*).

2. Determination of "Citrate-Soluble" Phosphoric Acid (Wagner's Method).—For this determination a 500 c.c. graduated flask having a neck not less than 2 cm. in diameter, with a capacity of at least 8 c.c. above the mark, is required.

5 grs. of the sample are placed in the flask and moistened with 5 c.c. of alcohol. The flask is then filled to the mark with a 2 per cent. standard solution of citric acid (prepared from fresh crystals, free from efflorescence) at a temperature of 17·5° and, after inserting the rubber stopper, the mixture is shaken for half an hour. (In commercial laboratories a rotary apparatus making thirty to forty revolutions per minute is employed for this purpose.) If the temperature of the room be not approximately 17° to 18° C., the flask should be insulated by enclosing it in a metal case lined with felt. After shaking, the solution is immediately passed through a large *dry* folded filter; 100 c.c. of the filtrate are mixed in a 250 c.c. flask with 10 c.c. of concentrated nitric acid and evaporated to about 25 c.c. After cooling, 25 c.c. of concentrated sulphuric acid are added and the

mixture again boiled for ten minutes. The solution is then carefully diluted to the mark with water and filtered. To 125 c.c. of this filtrate are added successively 30 c.c. of ammonium citrate solution, 30 c.c. of 24 per cent. ammonium hydrate, and (after cooling) 25 c.c. of magnesia mixture, and the whole stirred for one hour.

The above method is purely conventional and the analysis should be performed exactly as described, since the amount of phosphoric acid extracted from the basic slag depends largely upon the temperature, the time occupied in shaking, and other conditions. The concentration of citric acid is fixed at 2 per cent., to correspond with the *average* acidity of plant roots.

The object of evaporating the extract with concentrated nitric acid and treating with concentrated sulphuric acid, as described above, is to precipitate any trace of dissolved silica, which otherwise would be thrown down with the magnesium phosphate on adding ammonia.

" Basic slag " is obtained as a by-product in the manufacture of steel from phosphatic pig iron. In the " basic process " of Thomas and Gilchrist the molten pig iron is blown with air in converters, which are lined with a basic material prepared from ground dolomite and tar, and contain a charge of freshly burnt lime. On passing the blast, the phosphorus is oxidized to pentoxide, P_2O_5, and combines with the lime, forming a slag which floats upon the surface of the molten iron. The composition of this slag varies according to the amount of phosphorus, silicon, manganese and other impurities in the pig iron and the quantity of lime used. According to Schucht, the slags contain on an average 12 to 20 per cent. P_2O_5, 30 to 50 per cent. CaO, 2 to 20 per cent. SiO_2, 4 to 30 per cent. Fe_2O_3 and FeO, 3 to 15 per cent. MnO, 2 to 6 per cent. MgO, together with traces of sulphur and vanadic acid.

Owing to the high percentage of bases present, Thomas slags cannot be profitably treated with sulphuric acid. Fortunately, the major portion of the phosphate exists in a form soluble in citric acid, so that the slag after grinding in ball mills to a fine powder can be employed as a fertilizer.

The citrate-soluble calcium phosphate in slag is supposed to be the salt of an octabasic acid, $H_8P_2O_9 (= P_2O_5 + 4H_2O)$, having the formula $Ca_4P_2O_9 (= P_2O_5.4CaO)$. The fact has also been discovered that if a small quantity of sand or other siliceous substance is mixed with the slag in the converter during the blast, the solubility (in citric acid) of the resulting phosphate is considerably increased. This may be due to the formation of a soluble complex phosphosilicic acid, as indicated by the fact that on extracting the phosphate with citric acid a considerable amount of silica passes into solution at the same time. According to Schucht, however, the action of the sand is merely to form calcium orthosilicate, which then interacts with the tricalcium phosphate, converting it into tetracalcium phosphate in accordance with the equation

$$Ca_3(PO_4)_2 + Ca_2SiO_4 = Ca_4P_2O_9 + CaSiO_3.$$

The manufacture of basic slag is an important industry in Germany, where the principal ore (viz., minette) used for the production of iron contains a considerable amount of phosphorus. In England the consumption of this fertilizer is increasing. The price of basic slag depends upon the percentage of citrate-soluble phosphate, which is determined by Wagner's method as described above.

Phosphoric acid combined in this form commands a somewhat lower price than that in superphosphates, owing to the fact already mentioned that the manurial value of citrate-soluble phosphate is less than that of the water-soluble substance.

Basic slag also undergoes slight reversion if stored for a very long period. The tetracalcium phosphate is acted upon by the carbon dioxide of the air, and converted into insoluble tricalcium phosphate according to the equation

$$Ca_4P_2O_9 + CO_2 = Ca_3(PO_4)_2 + CaCO_3.$$

16. ORGANIC MANURES AND MIXED MANURES.

1. Determination of Potash—(*a*) *Organic Manures.*—10 grs. of the sample are ignited at *dull-red* heat in a platinum or porcelain dish; the ash is moistened with hydrochloric acid and evaporated to dryness on a water-bath. The residue is then rinsed with hot water into a 250 c.c. graduated flask and heated for some minutes by immersing the flask in boiling water. After cooling, the solution is diluted to the mark.

(*b*) *Inorganic Mixed Manures.*—10 grs. of the sample are boiled for fifteen minutes with 150 c.c. of water in a 250 c.c. graduated flask; the solution is allowed to cool and diluted to the mark with water.

100 c.c. of the solution from (*a*) or (*b*) are heated to boiling in a 200 c.c. graduated flask, and finely ground barium hydroxide is added until the liquid shows a strongly alkaline reaction. After allowing to cool, the solution is diluted to the mark and passed through a *dry* filter; 100 c.c. of the filtrate are transferred to a 200 c.c. graduated flask, mixed with excess of ammonium carbonate, and heated for thirty minutes by immersing in a bath of boiling water; the mixture is then cooled, made up to the mark, and again filtered; 100 c.c. of this filtrate are evaporated to dryness in a platinum dish and ignited gently to expel the ammonium salts; the residue is then taken up with a small volume of hot water, filtered into a porcelain dish, and the potassium determined either by the " platinic chloride " or the perchlorate method (pp. 119 and 120).

On adding barium hydroxide, the sulphuric and phosphoric acids are precipitated, together with the whole of the bases, such as iron, aluminium and magnesium. In this case, however, unlike the corresponding determination of potash in Stassfurt salts (p. 120), the excess of barium must be removed by the addition of ammonium carbonate.

In the case of mixed manures rich in sulphates it is advisable, before adding barium hydroxide, to acidify the solution slightly with dilute hydrochloric acid, heat to boiling, and precipitate the sulphuric acid by the addition of barium chloride; then, without filtering off the barium sulphate, make strongly alkaline with barium hydroxide.

2. Determination of Phosphoric Acid in Organic Manures.—10 grs. of the substance, contained in a 500 c.c. graduated flask, are moistened with a little water and then boiled with 50 c.c. of concentrated sulphuric acid for thirty minutes. After cooling, 20 c.c. of fuming nitric acid are carefully added and the solution boiled until it is quite colourless. It is then again cooled, diluted to the mark with water, and filtered; 50 c.c. of the filtrate are mixed with 50 c.c. of ammoniacal citrate solution (p. 127) and 25 c.c. of magnesia mixture, and stirred for thirty minutes in the usual way.

Organic manures containing phosphorus can also be treated with aqua regia, as in the determination of the total phosphoric acid in superphosphates (p. 127), but the organic matter is more rapidly and completely decomposed by successive treatment with concentrated sulphuric acid and fuming nitric acid, as described above.

3. Determination of Nitrogen—(*a*) *In Organic Fertilizers* (*Kjeldahl's Method*).—2 grs. of the substance, contained in a flask of resistance glass, are mixed with about 1 gr. (1 drop) of metallic mercury and 20 c.c. of pure concentrated sulphuric acid (free from nitrogen compounds). The flask is heated moderately until a uniform dark brown solution is obtained; this should be the case after about fifteen minutes; 15 to 20 grs. of chemically pure potassium sulphate are then added and the mixture heated strongly on a sand-bath until the sulphuric acid boils vigorously. A pear-shaped glass stopper should be placed loosely in the mouth of the flask to prevent the loss of acid by evaporation. Many substances froth freely at the outset; in such cases the potassium sulphate should be added at a later stage and the heat applied very gradually. Violent frothing can generally be moderated by adding a little paraffin wax.

The boiling is continued until the liquid has become quite colourless, generally two to three hours. After cooling, the contents of the flask are diluted with about 150 c.c. of water and the whole washed into a distillation flask such as that used in the determination of nitre in Chile saltpetre by Devarda's method (p. 90).

100 c.c. of 30 per cent. caustic soda and 30 c.c. of 4 per cent. potassium sulphide solution are then added, the head-piece inserted rapidly, and the mixture distilled for thirty minutes. The ammonia is absorbed in $\frac{1}{5}$ normal sulphuric acid. After cooling, the excess of acid is titrated back with $\frac{1}{5}$ normal caustic soda, using *methyl orange* as indicator (*cf*. note, p. 91).

As a rule the result is calculated in terms of nitrogen per cent., but in the case of organic substances containing this element solely in the form of albumin the result is conveniently expressed in terms of albumin or protein. The amount of nitrogen in the different kinds of albumin is fairly constant —viz., about 16 per cent.—hence the percentage of albumin in a substance may be calculated from that of nitrogen by multiplying by $\frac{100}{16} = 6{\cdot}25$. The nitrogen in miller's waste, such as wheat-bran and rye-bran, as also in by-products from oil-factories—*e.g.*, coconut cake, linseed and poppy-seed cake, which are used for feeding cattle—should always be stated in terms of protein.

In general, when an organic nitrogenous compound is boiled with concentrated sulphuric acid the whole of the nitrogen is converted into ammonium sulphate, while the carbonaceous matter is oxidized to carbon dioxide, with the simultaneous reduction of the sulphuric acid to sulphur dioxide. Small quantities of mercury salts accelerate this reaction catalytically, possibly by forming intermediate mercury-nitrogen compounds. The addition of potassium sulphate raises the boiling-point of the sulphuric acid, thereby increasing the rate of decomposition. When the decomposition is complete, caustic soda is added to liberate the ammonia from the ammonium sulphate produced.

The addition of potassium sulphide serves to break up complex mercury-ammonia compounds formed by the combination of free ammonia with the mercuric oxide which is precipitated by the excess of caustic soda:

$$NH_4OH + 2HgO = NHg_2OH + 2H_2O,$$

and

$$NHg_2OH + 2K_2S + 3H_2O = 2HgS + 4KOH + NH_3.$$

These complexes, which may be regarded as ammonium compounds in which the hydrogen of the ammonia is replaced by divalent mercury, are not completely decomposed by caustic soda even on boiling, so that the percentage of nitrogen found is too low. By treatment with potassium sulphide, however, the whole of the nitrogen is recovered as ammonia.

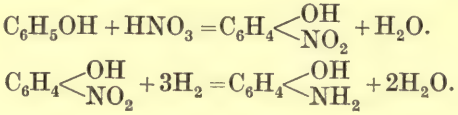
According to Böttcher, 1 to 2 grs. of zinc dust may be substituted for potassium sulphide, since nascent hydrogen reduces the complexes to ammonia and metallic mercury. A disadvantage of this method is that mercury is slightly volatile in steam, for which reason the distillation has to be conducted in a draught chamber.

The above method may be used for the determination of nitrogen in all kinds of organic substances, provided not more than a trace of this element is present in the form of nitrate. Small quantities of nitrate are reduced to ammonia by the carbon formed during the decomposition with sulphuric acid.

If the amount of nitrogen in the form of nitrate exceeds 5 per cent. of the total nitrogen present, the following modification of Kjeldahl's method is adopted:

(*b*) *In Mixed Manures containing Nitrate* (*Iodlbauer's Method*).—0·5 to 1 gr. of the sample (to contain not more than 0·1 gr. of nitrate nitrogen) is ground up with 2 to 3 grs. of anhydrous gypsum and placed in a Kjeldahl flask; 30 c.c. of concentrated sulphuric acid containing 4 grs. of phenol per 100 c.c. are added (with cooling) and the flask is shaken vigorously until the contents are uniformly mixed, after which it is set aside for about fifteen minutes: 2 to 3 grs. of zinc dust are then gradually added, followed by 1 drop of mercury, the flask being well cooled during the addition. After allowing to stand for thirty minutes, potassium sulphate is added and the mixture boiled for three or four hours, as described under (*a*).

By the addition of phenol the nitrate-nitrogen is converted into nitrophenol, which is then reduced by the zinc to amidophenol:



$$C_6H_5OH + HNO_3 = C_6H_4{<}\substack{OH \\ NO_2} + H_2O.$$

$$C_6H_4{<}\substack{OH \\ NO_2} + 3H_2 = C_6H_4{<}\substack{OH \\ NH_2} + 2H_2O.$$

The nitrogen in the amido- form is then converted quantitatively into ammonium sulphate, as before, by boiling with sulphuric acid in presence of mercury salts.

The object of mixing with gypsum is to prevent hydrous substances from being too strongly heated on treatment with concentrated sulphuric acid and phenol.

The most important organic fertilizer is farmyard manure, but this is rarely submitted to analysis. For some years Peruvian *guano* of comparatively recent origin, containing phosphorus in a readily assimilable form, together with 10 to 15 per cent. of nitrogen, was extensively used, but the supplies have been exhausted. The various guanos now on the market are mostly mineralized, and contain hardly any organic matter.

Other organic manures, which are often of great value, though obtainable in relatively small quantities, include bats' guano, found in the caves of Sardinia, and the various artificial guanos, such as *fish guanos,* prepared from the offal and residues of the cod-drying industry; *bone-meal,* containing about 4 per cent. nitrogen; and *flesh-meal,* prepared from slaughter-house waste. The latter is treated with superheated steam, dried and pulverized. Blood, horn and leather waste are worked up respectively into blood-meal and leather-meal. There are also numerous mixed manures in the market—*e.g.*, ammonium superphosphate, prepared by mixing ammonium sulphate with superphosphate. "Potato manure" is composed of superphosphate, Chile saltpetre, ammonium sulphate and blood-meal or horn-meal. Of recent years mixed phosphorus-potash fertilizers have been made by heating phosphates with carnallite.

17. IRON ORES.

An average sample sufficient for all the following determinations is reduced to a very fine condition in an agate mortar.

1. Determination of Moisture.

About 5 grs. of the ore are heated at 100° to 105° C. until constant in weight and the loss determined.

The drying temperature should not exceed 105°, otherwise such ores as bog-iron ore and limonite may lose water of hydration.

2. Determination of Iron.

0·5 to 0·8 gr. of the ore are ignited for a few minutes at dull redness in a large porcelain crucible. After cooling, 10 to 15 c.c. of concentrated hydrochloric acid (sp. gr. 1·19) are added and the mixture heated until the residue of silica (if any) is perfectly white. Should the residue be dark in colour or have a reddish tint, a few drops of hydrofluoric acid are added and the heating continued for a short time (Ledebur). If this treatment be not effective, the residue must be separated on a small filter, ignited, and fused with a little sodium potassium carbonate mixture in a platinum crucible. The fused mass is dissolved in a small quantity of water, the solution acidified with hydrochloric acid in a tall covered beaker and, without filtering, added to the original solution.

The liquid is then heated to boiling, and a solution of stannous chloride (prepared by dissolving 25 grs. of the pure salt in concentrated hydrochloric acid and diluting with water to 250 c.c.) is added drop by drop until the colour is just discharged. After cooling, 10 c.c. of a saturated solution of mercuric chloride are added, the liquid is diluted to about 800 c.c. with freshly boiled water, and treated with 10 c.c. of a manganese mixture prepared in the following way: A solution of 15 grs. of crystalline manganous sulphate in 100 c.c. of water is mixed with 25 c.c. of concentrated sulphuric acid, followed by 30 c.c. of concentrated phosphoric acid, and diluted to 200 c.c.

The contents of the flask are then titrated with permanganate until a pink coloration is obtained, which persists for several seconds. The change of colour is best observed if the titration be done in a porcelain dish.

The object of igniting the ore is to destroy any organic matter, which otherwise would consume permanganate in the subsequent titration. The use of stannous chloride as a reducing agent for iron is preferred in commercial analysis on account of its simplicity, but the reaction takes place rapidly and completely only in hot, strongly acid solution—

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

The progress of the reduction is shown by the gradual discharge of the deep yellow colour of the ferric chloride. Towards the end the velocity of the reaction diminishes; the stannous chloride should then be added very slowly, the solution being well stirred and a few seconds allowed to elapse between successive additions.

Mercuric chloride is added to remove any excess of stannous chloride—

$$2HgCl_2 + SnCl_2 = SnCl_4 + Hg_2Cl_2.$$

Not more than a faint cloud of lustrous white mercurous chloride should be produced for the titration to be successful. If any considerable quantity of a white or grey precipitate (containing metallic mercury) be formed, the end-point of the titration is obscured, owing to the reduction of permanganate by the excess of mercurous chloride.

While hydrochloric acid is practically unaffected by permanganate in dilute aqueous solution, the presence of ferrous salts causes the evolution of chlorine; this, however, may be prevented by adding a small amount of manganese salt to the solution. The observation of the end-point is facilitated by the addition of phosphoric acid, which combines with the ferric chloride to form *colourless* acid ferric phosphate, whereby the strong yellow colour of the solution is discharged.

3. Determination of Manganese (Volhard's Method).

A suitable weight of the sample (0·6 to 1 gr. of true manganese ores, 3 grs. of calcined spathic iron ores, or 5 grs. of other iron ores) is dissolved in concentrated hydrochloric acid (sp. gr. 1·19), using 20 c.c. of the acid for every 1 gr. of ore and proceeding as in the determination of iron (2). If the ore contains ferrous oxide, the solution should be cooled and a little potassium chlorate cautiously added (about 0·15 gr. for every 1 gr. of ore) and the mixture heated until the iron has been completely oxidized and any excess of chlorate destroyed. A small quantity of water is then run in and the solution boiled to expel the free chlorine.

After cooling, the solution is transferred to a 500 c.c. graduated flask and diluted to the mark with water. For each titration 100 c.c. of this solution are pipetted into an Erlenmeyer flask of about 1½ litres capacity and diluted to 600 to 700 c.c. with water. It is then heated to about 70° to 80° C., and zinc oxide made into a thin paste with water, is added until the solution curdles—*i.e.*, until the iron is precipitated as hydroxide in large flakes, while the solution itself remains colourless and transparent—after which a slight excess of the paste is added. The mixture (without filtering) is then rapidly heated to boiling and titrated with permanganate until a faint pink coloration is produced, the flask being shaken vigorously after every addition. In order to obtain a clear indication of the end-point, the boiling should be interrupted from time to time and the dark precipitate allowed partially to subside, this generally requiring only a few seconds. The pink coloration should not disappear even after prolonged shaking.

When neutral solutions of manganous salts containing basic compounds of magnesium, calcium or zinc are titrated with permanganate, the latter is reduced and the manganous salts are oxidized simultaneously to *tetravalent* manganese compounds which combine with the bases present, forming salts of variable composition (see under Weldon Mud, p. 117). The changes which take place are indicated in the following equation:

$$4KMnO_4 + 6MnCl_2 + 9Zn(OH)_2 = 5Zn(HMnO_3)_2 + 4KCl + 4ZnCl_2 + 4H_2O.$$

The zinc oxide added must be quite pure; it should be tested before use and should not show any reducing action on permanganate. Any ferrous oxide present in the ore, which would also consume permanganate, must be converted to the ferric condition before titrating.

In calculating the result, note that in this titration the permanganate is reduced only to MnO_2. Hence 2 molecules of permanganate yield but 3 atoms of oxygen, as compared with 5 atoms of oxygen in the acid reduction to MnO. The titre of the permanganate should therefore be multiplied by $\frac{3}{5}$.

Manganese is associated with all iron ores. *Spathic iron* ($FeCO_3$) is especially rich in the isomorphous carbonate of manganese, $MnCO_3$. In certain ores—*e.g., manganite,* MnO(OH), isomorphous with *goethite,* FeO(OH)—the manganese exists in the trivalent condition corresponding to that of iron. There are also isomorphous compounds which contain both divalent and trivalent iron together with divalent and trivalent manganese—*e.g., manganese-magnetite,* $Fe''Mn''(Fe'''Mn'''O_2)_2$. Besides the manganiferous iron ores, true manganese ores are also used in the iron industries for the preparation of ferromanganese and spiegeleisen (specular cast iron); the most important of these are *pyrolusite,* MnO_2, and *wad,* which consists of pyrolusite and hydrated manganous oxide.

4. Determination of Arsenic.

5 grs. of the ore are mixed with 3 to 5 grs. of potassium chlorate (according to the amount of ferrous oxide present) and heated in a beaker with 80 c.c. of concentrated hydrochloric acid, at first gently, and finally at boiling-point to expel the chlorine completely. The solution is carefully decanted from the residue into a distillation flask provided with a tap funnel and connected with a sloping condenser (Fig. 30). A few beads or fibres of glass wool may be placed in the flask to prevent bumping. Should the gangue remaining in the beaker not be perfectly white, it must be treated again with a little potassium chlorate and hydrochloric acid, and finally washed into the flask with the least possible quantity of concentrated hydrochloric acid. A solution of 5 grs. of ferrous chloride in 30 c.c. of concentrated hydrochloric acid is then added from the funnel, and the mixture distilled into a beaker until only about

20 c.c. remain in the flask. After allowing the flask to cool somewhat, a further 50 c.c. of hydrochloric acid (previously warmed as a precaution against cracking the glass) are added, and the distillation repeated until only 20 c.c. of the mixture remain. The acidic distillate is then nearly neutralized with sodium carbonate, treated with an excess of sodium *bicarbonate*, and titrated with iodine solution, using starch as indicator.

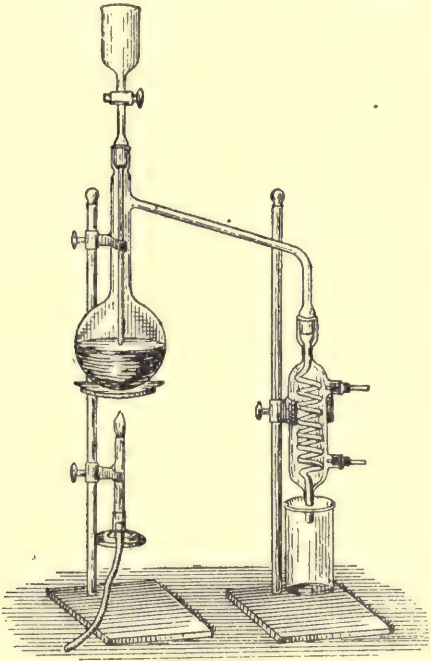


FIG. 30.

In opening up the ore, potassium chlorate is added to prevent the formation, at this stage, of volatile arsenious chloride, $AsCl_3$, by bringing the arsenic completely into solution as non-volatile arsenic acid, H_3AsO_4. (A pentachloride does not exist.) By the subsequent addition of ferrous chloride, the arsenic acid is reduced to arsenious acid, which is converted in the flask into arsenious chloride by the large excess of concentrated hydrochloric acid present, according to the equation

$$H_3AsO_3 + 3HCl \rightleftharpoons AsCl_3 + 3H_2O.$$

The volatile arsenious chloride distilling over is condensed, and collected in the receiver. On adding a base to the acidic distillate, arsenious acid is again formed, and is then titrated with iodine.

The titration of arsenious acid with iodine proceeds to completion only when an excess of sodium bicarbonate is present. In *acid* solutions the reaction is reversible, a certain amount of the arsenic acid formed being reduced by the hydriodic acid:

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2HI.$$

On the other hand, the solution cannot be made *alkaline*, since in this case the hydroxyl ion would react with iodine to form iodate:

$$3I_2 + 6OH' = IO_3' + 5I' + 3H_2O.$$

In the presence of sodium bicarbonate, however, the hydriodic acid is neutralized as fast as it is formed, thus permitting the quantitative oxidation of the arsenious acid.

As a rule not more than a trace of arsenic occurs in iron ores, but occasionally magnetic iron ore contains a considerable amount of *arsenical pyrites*, FeAsS. Such ores are unsuitable for smelting, since in the blast furnace any arsenic is taken up by the iron, from which it cannot afterwards be removed. For this reason, according to Ledebur, many kinds of iron contain minute traces of arsenic, which, however, do not appreciably affect the properties of the metal. Larger amounts of arsenic (even as little as 0·1 per cent), like phosphorus, render the iron "cold-short" and, like sulphur, "red-short."

5. Determination of Titanium.

1 to 5 grs. of the ore, contained in a Rose crucible, are reduced at bright red heat in a current of hydrogen previously dried by passing through a wash-bottle of concentrated sulphuric acid. After allowing the crucible to cool, with the hydrogen still passing, the contents are transferred to a beaker and boiled with very dilute sulphuric acid (1 : 40) until the evolution of gas ceases; 40 c.c. of the dilute acid are used for every gram of the ore weighed out. The residue is filtered, and ignited on the filter in a platinum crucible.

A small quantity of concentrated sulphuric acid, followed by hydrofluoric acid in the proportion of 9 of the latter to 4 of the former, is then added and the silica volatilized by evaporating to dryness on a sand-bath and finally igniting. The residue is heated with a little sodium potassium carbonate; the fused mass is extracted with water, filtered, and the insoluble matter ignited on the filter in a platinum crucible. This residue is fused with about 6 grs. of potassium bisulphate in a covered platinum crucible at dull redness for one hour. The melt is dissolved in about 200 c.c. of *cold* water, an operation which requires several hours. The solution is then saturated with hydrogen sulphide, by which the iron is reduced to the ferrous condition and any copper present, as also traces of platinum derived from the crucible, are precipitated. The suspension is transferred to a 300 c.c. graduated flask and made up to the mark with water; 250 c.c. are passed through a *dry* filter into an ordinary flask, diluted with an equal volume of water, and boiled for about one hour, any water lost being replaced by occasional additions. The white precipitate is allowed to settle, filtered, washed thoroughly with hot water, ignited, and weighed as TiO_2.

For the determination of titanium it is necessary first to remove most of the iron. If the ores were treated with concentrated hydrochloric acid in the usual way, a large amount of the titanium also would pass into solution as $TiCl_4$. For this reason the iron oxide in the ore is first reduced to metallic iron, which is then dissolved in sulphuric acid of such dilution that the titanium is not attacked. The residue, freed from silica by treatment with hydrofluoric acid, is then fused with sodium carbonate to remove the phosphoric acid, which on treatment with water passes into solution as alkali phosphate, while the titanium remains as insoluble Na_2TiO_3. The latter, on fusion with potassium bisulphate, forms titanic sulphate, $Ti(SO_4)_2$, which must be dissolved in *cold* water, since on heating in neutral or slightly acid solution it undergoes hydrolysis, like all titanium salts, with the separation of titanic acid, thus:

$$Ti(SO_4)_2 + 3H_2O = H_2TiO_3 + 2H_2SO_4.$$

This property of titanic sulphate is utilized for the quantitative separation of titanic acid.

The precipitate of titanic acid is only obtained perfectly free from iron when the amount of the latter present in the solution is very small and it exists in the ferrous condition.

Titanium is found very frequently in iron ores. An exceptionally high percentage of this element is a characteristic feature of many of the magnetic iron ores of Scandinavia and North America. It generally occurs, not in the form of TiO_2, but as trivalent Ti_2O_3, isomorphous with Fe_2O_3. Thus, the *titaniferous iron glances* or *specular iron ores* may be regarded as $(FeTi)_2O_3$, while the *titaniferous magnetic iron ores* are looked upon as titano-magnetites, $Fe(Fe.TiO_2)_2$. When these ores are treated with concentrated hydrochloric acid, or fused with sodium carbonate, the titanium is oxidized by the ferric oxide to the tetravalent form as $TiCl_4$ or Na_2TiO_3, a corresponding amount of ferrous oxide being formed at the same time.

In the smelting of iron ores titanium, if present in any considerable amount, renders the slag infusible.

6. Determination of Chromium.

0·3 to 1 gr. of the ore is mixed in a porcelain crucible with 4 to 8 grs. of sodium peroxide and fused at a moderately low temperature (the mass should not be red-hot). After allowing to cool, the fused mass is extracted with cold water, then heated with water at about 90° C. for thirty minutes and finally, when cold, acidified slightly with sulphuric acid. Everything should pass into solution except the silica, which remains as a white precipitate. The solution, in which the whole of the chromium is now present as chromic acid, is cooled and either (*a*) titrated directly with decinormal ferrous ammonium sulphate by the spot method, using potassium ferricyanide as indicator, or (*b*) mixed with an excess of decinormal ferrous ammonium sulphate and titrated back with permanganate.

The object of heating the solution of the fused substance *before* adding sulphuric acid is to decompose any excess of sodium peroxide. Otherwise, on acidifying, hydrogen peroxide would be formed; this would convert the chromic acid into the blue perchromic acid $HCrO_5$, which readily passes into chromic salt, with evolution of oxygen, thus rendering the subsequent titration worthless.

True iron ores do not contain chromium. In the iron industries, however, chromium ores are worked up into ferrochrome, which is added to steel to increase the tenacity. The only chromium ore of commercial importance is *chromite* (chrome ironstone), which is composed of ferrous oxide and chromic oxide, $FeO.Cr_2O_3$, isomorphous with spinel. It occurs abundantly in the Ural Mountains, Silesia, North America and elsewhere.

With the exception of aluminium, iron is the most widely distributed metal in the crust of the earth. Not all of its ores, however, are suitable for smelting, and the term "iron ore" might properly be restricted to the oxides, hydroxides, and carbonates. The sulphides—*e.g.*, pyrites—only become available for the production of metallic iron after the sulphur has been roasted off and foreign metals such as copper and zinc have been removed. Iron ores are obtained chiefly underground by blasting, though occasionally they are quarried in open cuts, as, for instance, the immense deposits of red hæmatite near Lake Superior and the minettes of Luxemburg.

The most important iron ores are the following:

(1) **Oxides.**—(*a*) *Magnetite,* Fe_3O_4, so called from its magnetic properties, is isomorphous with spinel, $MgO.Al_2O_3$, and may therefore be regarded as ferroferrite, $FeO.Fe_2O_3$. One-third of the iron is thus present in the form of ferrous oxide (basic), the other two-thirds as ferric oxide (acid). This ore is in great demand on account of its comparative freedom from phosphorus. Vast deposits occur in Northern Sweden (Lapland); to a less extent it is found also in Norway, Russia (Urals) and North America. Small quantities are also mined in the Erzgebirge of Saxony and in the Hartz Mountains. Of all the ores of iron this is the most difficult to reduce, but it is improved by a preliminary roasting, in which the ferrous oxide is converted into ferric oxide.

(*b*) *Hæmatite,* Fe_2O_3, is a pure oxide which is found in various forms:

(i.) Crystalline, as *iron glance* (specular iron ore or micaceous iron ore). The famous iron glance of Elba has been worked from the earliest times.

(ii.) In masses of kidney-shaped or grape-like aggregates, as *kidney iron ore.*

(iii.) Ordinary compact or earthy red iron ore (*red ochre*). Immense deposits of very pure compact red iron ore occur round Lake Superior and form the principal raw material in the smelting industry of the United States. England also possesses important supplies of this mineral in Cumberland and North Lancashire, while large quantities are obtained in the province of Biscay, in Spain. The red iron ores also contain very little phosphorus, and are much sought after for smelting.

(2) **Hydroxides.**—*Brown Iron Ores.*—These ores are distinguished from the preceding by their brown or yellow colour and differ from them chemically in the amount of combined water which they contain. This varies very considerably, corresponding in most cases to a mixture of different hydrates, of which three are distinguished by mineralogists—viz.:

$Fe(OH)_3 - H_2O = FeO(OH)$, gœthite
$2Fe(OH)_3 - H_2O = FeO(OH)_4$, xanthosiderite.
$4Fe(OH)_3 - 3H_2O = Fe_4O_3(OH)_6$, limonite.

Brown iron ore is also found in several varieties:

(i.) *Brown hæmatite*, like red hæmatite, occurs in kidney-shaped aggregations. It is the purest of the brown ores, but is found in such small quantities that it possesses little economic importance.

(ii.) Ordinary *brown ironstone* is very widely distributed and is found both in an extremely pure condition and also contaminated with quartz, clay, pyrites, glance and phosphates.

(iii.) *Pea ores* and *oolitic ores* occur as rounded granules, 2 to 20 mm. in diameter, either loose as rubble or conglomerated with quartz or clay and usually interspersed with nodules of apatite. Enormous deposits of these ores are found in Hanover. An especially fine-grained pea ore, also rich in phosphorus, is known in Luxemburg as " minette." The minettes of Lorraine and Luxemburg attain in places a thickness of 20 metres.

(iv.) *Bog iron ore*, also known as marsh ore, meadow ore and umber. These terms are applied to deposits of iron hydroxide which occur in flat, swampy country, either in an earthy form or in hard masses. They are mostly interspersed with quartz and ferrous phosphate [*vivianite*, $Fe_3(PO_4)_2.8H_2O$]. Bog ores are found all over the North German Plain, in Ireland, Holland and Russia. (For the use of these ores in the purification of coal gas see p. 70.)

The brown iron ores, after calcination, are characterized by easy reducibility, due to the fact that they are much less dense than the magnetic and red ores.

(3) **Carbonates.**—*Spathic iron ore*, $FeCO_3$, is a *ferrous* material. It generally contains a considerable amount of isomorphous minerals, such as calcspar, $CaCO_3$, magnesite, $MgCO_3$, diallogite,

$MnCO_3$, and less frequently calamine, $ZnCO_3$, but is almost always free from phosphorus. From the earliest times spathic iron ore has been much in demand for the preparation of manganiferous iron free from phosphorus. The roasted ore is reduced with extreme ease.

Several varieties are distinguished:

(i.) Crystalline spathic iron ore is the purest but rarest variety. The German spathic ores of Siegerland have been famous for centuries. Other noteworthy deposits are found in Styria, Carinthia and Hungary.

(ii.) *Clay ironstone,* or *spherosiderite,* consists of a mixture of spathic ore, partially weathered to brown ore, with clay. It is the most important raw material used for smelting in the North of England.

(iii.) *Blackband ironstones* are mixtures of spathic ores or clay ironstones with 10 to 25 per cent. of black coal. They occur particularly in Scotland and Staffordshire.

18. IRON.

The sample of iron is carefully freed from scale and rust. A quantity sufficient for the analysis is rasped off with a file previously cleansed with ether. Samples of tempered steel should first be softened by annealing. As the carbon content is liable to be affected by heating, this should be done in absence of air. Ledebur recommends heating in molten lead.

1. Determination of Carbon.

(*a*) **Gravimetric (Särnström's Method).**—1·5 grs. of cast iron, or 3 grs. of malleable iron, are taken for the analysis. The reagents required are (1) Chromic acid solution: an aqueous solution of chromic acid saturated in the cold is boiled with a few drops of concentrated sulphuric acid in a flask for about half an hour to destroy any organic matter present; after cooling, it is kept in a well-stoppered bottle. (2) Sulphuric acid: concentrated sulphuric acid (sp. gr. 1·84) is diluted with an equal volume of water.

The apparatus employed is shown in Fig. 31. The sample of iron is treated in the flask *b* with a mixture of the prepared sulphuric and chromic acids, by which the carbon is converted into carbon dioxide. This is freed from acid vapour by a condensing arrangement in the neck of the flask, and then passes through a platinum tube *c* heated to redness, where any traces of hydrocarbons which have escaped oxidation by the chromic acid are burnt completely to carbon dioxide and steam. The carbon dioxide is freed from moisture by passing through the calcium chloride tube *d*, and is then absorbed in the tared **U**-tube *e*, which contains soda lime, followed by a layer of calcium chloride. The guard tube *f*, containing calcium chloride, is used to prevent access of moisture from the suction pump connected with this end of the apparatus. During the whole experiment a current of air, washed with dilute potash solution in *a*, is drawn through the apparatus. In place of the platinum tube an ordinary combustion tube of hard glass 40 to 50 cm. in length, charged with copper oxide and heated to redness in a small furnace, may be used.

With the soda-lime tube detached, a few litres of air are drawn through the apparatus. The tared **U**-tube is then connected up. The sample, contained in a small glass tube, is placed in the empty flask *b* and the condenser fixed in position. The stopper in the side limb of the flask is then raised and 20 c.c. of chromic acid admitted from the funnel.

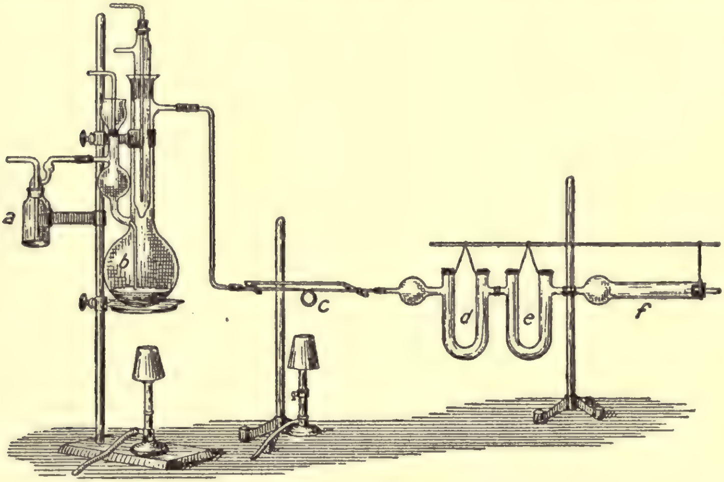


FIG. 31.

When this has drained into the flask, 150 to 200 c.c. of sulphuric acid (150 c.c. for cast iron, 200 c.c. for wrought iron) are admitted in the same way. After replacing the stopper, the air current is turned on, and the flask heated gently over a Bunsen burner. During the heating the flask should be well shaken until the chromic acid, which has been thrown out of solution by the addition of sulphuric acid, is redissolved. This precipitate tends to stick to the bottom of the flask, which, in consequence, is liable to become overheated and crack. The mixture is kept in a state of gentle ebullition for two and a half hours. The soda-lime tube is then disconnected and weighed. From the increase in weight, due to the absorbed carbon dioxide, the percentage of carbon originally present in the iron may be calculated.

(*b*) **Colorimetric (Eggertz and Spüller's Method).**—This method is suitable for certain kinds of malleable iron—*e.g.*, wrought iron—but not for cast iron. A number of samples of soft iron containing known amounts of carbon (determined by the preceding method) are required for comparison; 0·1 gr. of the standard iron and of the sample under investigation are taken for the analysis. The weighed samples, contained in wide test-tubes, are treated with 5 c.c. of nitric acid (sp. gr. 1·18 to 1·2) free from chlorine, the tubes being placed in cold water until the first vigorous reaction has subsided. The test-tubes are then wiped with a dry cloth and immersed for five minutes in an oil-bath heated to 135° C., after which they are again cooled in water. The solutions prepared in this way are washed into measuring cylinders and diluted until they have the same tint, which is best observed by placing the glasses together in front of a sheet of white paper. The volume of the liquid in either tube should not be less than 8 c.c., so that the hue produced by the carbon is unaffected by the colour due to the ferric nitrate. Iron containing combined carbon dissolves in nitric acid of the above concentration, yielding a brown solution. The tint produced in the case of malleable iron is directly proportional to the amount of carbon present. Hence if equal amounts of a standard iron and of the sample under examination be dissolved and the solutions diluted until they have the same tint, the volumes of the solutions after dilution will give the relative percentages of carbon in the two samples.

Calculation: If c and c_1 represent the percentages of carbon in the standard iron and in the sample respectively, v and v_1 the volumes of the corresponding solutions, then $v : v_1 = c : c_1$, or $c_1 = \frac{v_1 \times c.}{v}$

Commercial iron invariably contains carbon, the amount of which exercises a profound influence on the physical properties of the metal. These data may be used to classify roughly the different varieties of iron:

(1) Iron containing less than about 0·3 per cent. of carbon is flexible. At a red heat it becomes so soft that it can be easily forged to any shape and for this reason is known as "wrought iron." Of the various kinds of iron this has the highest melting-point.

(2) Iron containing from 0·5 per cent. to about 1·6 per cent. can also be forged, but it has a quality not possessed by wrought iron—viz., that of hardening when suddenly cooled from a red heat by plunging it into oil or water. "Steel" is a variety of commercial iron which can be hardened in this way.

(3) When the amount of carbon exceeds about 2·3 per cent., the iron is brittle, melts without softening and can neither be forged nor hardened. It has the lowest melting-point of all the different varieties. This is called "cast iron." It is the first product of ore reduction and always contains, in addition to carbon, other impurities, such as phosphorus, sulphur, silicon and frequently also manganese.

The various kinds of carbon which occur in iron are distinguished as (1) *hardening* carbon, (2) combined or *carbide* carbon, (3) *graphitic* carbon, (4) *annealing* carbon. The conditions under which any one of these can exist and its influence on the metal are shown graphically in the diagram (Fig. 32). The temperatures are plotted as ordinates, the percentages of carbon as abscissæ. Pure iron melts at 1,540° C. By the addition of carbon the melting-point is diminished along the line AB to a minimum at 1,130° C., called the "eutectic point," corresponding to 4·3 per cent. of carbon; further addition of carbon raises the melting-point, as indicated by the line BC. At temperatures above the line ABC the substance is thus in a molten condition, and below this line it crystallizes out.

If the iron contains more than 4·3 per cent. of carbon, the latter separates out in the form of graphite when the temperature is reduced along the line CB. Similarly, in the case of molten iron containing less than 4·3 per cent. of carbon, pure iron might be expected to separate along the line AB. A solution of carbon in iron, however, belongs to that class of alloys in which, not the pure solvent, but a solid solution of the dissolved substance in the solvent, separates on cooling. Hence the iron which crystallizes along AB contains carbon in *solid solution.* The amount of carbon in this condition increases with the amount present in the liquid up to a maximum of 2 per cent.; the line AE represents the upper limit of the area in which this solid solution, termed *austenite*, can exist.

On further cooling, austenite exhibits various transformations, owing to the property possessed by the iron-carbon alloys of undergoing very marked structural change even in the solid state. With decreasing temperature, the solubility of the carbon in a state of solid solution diminishes. The carbon, however, does not separate as such, but the excess enters into chemical combination with the iron to form a carbide, Fe_3C, known as *cementite*. *EH* represents the equilibrium line between austenite and cementite, and indicates the boundary of the austenite area towards the right. When the solid austenite cools to temperatures along this line, conversion into cementite takes place, with evolution of heat. At the point *H* the percentage of carbon in the solid solution has fallen to 0·89 per cent. If the austenite contains less than 0·89 per cent. of carbon at the outset, no cementite can be formed; but when the line *FGH*, bounding the austenite area to the left, is reached, pure iron separates out along it, the austenite thus becoming richer in carbon up to 0·89 per cent.

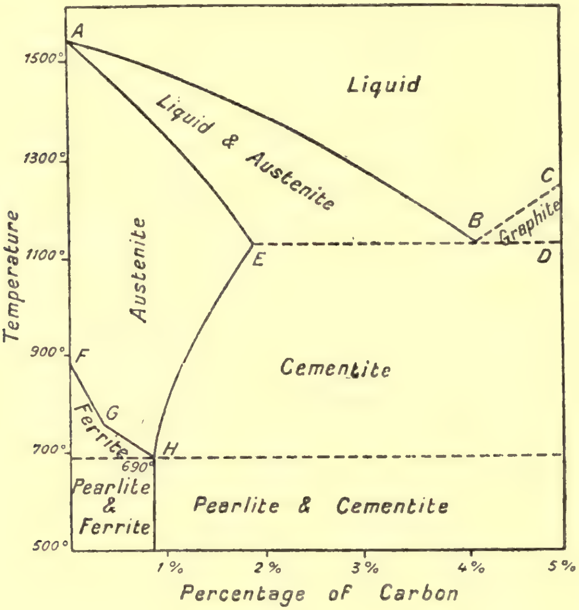


FIG. 32.

and attaining the point *H*. This iron, which separates in the crystalline condition, is termed *ferrite*. Below *H* (690° C.) a solid solution can no longer exist. The whole of the austenite remaining when this point is reached decomposes, with evolution of much heat, into pure iron and iron carbide—*i.e.*, into ferrite and cementite. As the solid solution of carbon always has the same concentration at $H (=0{\cdot}89$ per cent.), the same quantities of ferrite and cementite are produced by its decomposition. This eutectoid mixture has been given the name of *pearlite*, on account of its pearl-like appearance.

Malleable iron and steel thus consist at high temperatures of a homogeneous crystalline mixture of iron and carbon, which, on slowly cooling, splits up completely into pure iron and iron carbide. This decomposition, however, can be largely arrested by rapid cooling, and hardness is thereby imparted to the iron. The hardening of iron by sudden cooling is thus explained. It is less noticeable in malleable iron, because the solution is too dilute. The difference between malleable iron and steel is only one of degree. When liquids containing more than 2 per cent. of carbon solidify slowly, the excess of the latter separates in the form of *graphite*. Sometimes, however, especially when the process of solidification is rapid or if much manganese be present, the less stable product, cementite, is formed and remains in the metal. In the first case *grey cast iron* containing graphite is obtained, in the latter *white cast iron* containing carbide. Finally, if the white cast iron be submitted to prolonged heating at a high temperature, the cementite is decomposed, with separation of *annealing* carbon, which, however, unlike graphite, is amorphous.

Analytically the various kinds of carbon are distinguished as follows: Hardening carbon—*i.e.*, "martensitic carbon"—is soluble in dilute acid, with evolution of hydrocarbons; carbide carbon is insoluble in dilute acids, but is attacked by concentrated acids, also with the production of hydrocarbons; graphite and annealing carbon are not attacked by acids and remain unchanged after the iron has passed into solution.

2. Determination of Silicon and Phosphorus.

(*a*) **Silicon.**—About 3 grs. of grey cast iron (or 5 to 6 grs. of white cast iron or malleable iron) are dissolved in 50 to 75 c.c. of 30 per cent. nitric acid (sp. gr. 1·20) in a tall beaker immersed in cold water. When the first violent reaction has subsided, the beaker is heated until the iron is dissolved completely and the evolution of brown fumes has ceased. The contents of the beaker are then washed into a porcelain dish and evaporated to dryness on a sand-bath with constant stirring. Any hard crust sticking to the bottom of the dish is carefully scraped away, the whole residue is crushed to a loose powder, and then carefully heated to dull redness over a naked flame. The ignition is continued until the evolution of brown fumes ceases, when the conversion of the ferric nitrate into oxide is complete. After cooling, 50 c.c. of concentrated hydrochloric acid are added and the mixture heated until the iron oxide is completely dissolved; the solution is then evaporated to dryness on a water-bath. The residue is allowed to cool, moistened with hydrochloric acid and left for fifteen minutes, so that any basic salt formed during the evaporation may be reconverted into chloride; it is then taken up with water. The silica and graphite are filtered off, washed well with hot water, burnt moist on the filter in a platinum crucible, and ignited strongly to remove the carbonaceous matter. The residue after ignition is fused with about six times its weight of sodium potassium carbonate and a little potassium nitrate. The fused mass is cooled, decomposed with hydrochloric acid and twice evaporated with concentrated hydrochloric acid to dryness on a water-bath. Finally, the residue is taken up with hydrochloric acid and filtered. The whole of the silicon is now on the filter as silicic acid. It is burnt moist in a platinum crucible, ignited, and weighed as SiO_2.

When a sample of iron containing silicon is dissolved in nitric acid, the silicon is oxidized to silica. Phosphorus under the same treatment is oxidized to phosphorous acid, which on subsequent ignition is converted quantitatively into phosphoric acid. The residue remaining after the preliminary treatment with nitric acid invariably contains, besides graphite, a small quantity of iron or manganese, and fusion with sodium carbonate is necessary for the complete purification of the silica.

Silicon is produced in the blast furnace by the reduction of silica and forms an alloy with the iron. It is supposed that only the *free* silica, and not that combined with bases such as lime, manganese, or alumina, is reduced in this way. Hence it is possible to control the amount of silicon ultimately left in the pig iron by varying the quantity of lime added to the charge, whereby more or less of the silica is carried into the slag.

Only in wrought iron is the presence of silicon objectionable. In cast iron, on the contrary, it is often a desirable constituent, since the comparatively small amount present stimulates the separation of graphite when the metal solidifies, thus preventing the formation of white cast iron.

(*b*) **Phosphorus (Ledebur's Method).**—The hydrochloric acid filtrate from the silicon determination, containing iron, is diluted to a known volume, of which one-half to one-tenth, according to the amount of phosphorus present, is removed with a pipette and evaporated to dryness in a porcelain dish. The residue is dissolved in the least possible quantity of dilute nitric acid, and the solution mixed with 10 grs. of ammonium nitrate in 30 c.c. of water and 10 c.c. of 25 per cent. nitric acid (sp. gr. 1·15). The mixture is heated to boiling and treated with 80 c.c. of a 3 per cent. solution of ammonium molybdate previously warmed to about 90° C. After standing for twenty minutes, the yellow precipitate is filtered off and washed with 1 per cent. nitric acid until the washings, tested with ammonium thiocyanate, show no trace of iron. By means of a jet of distilled water the bulk of the precipitate is then washed off the filter-paper into an Erlenmeyer flask of about 50 c.c. capacity and the remainder is dissolved in the smallest possible quantity of ammonia; 10 grs. of pure zinc are then placed in the flask (not the *purest* zinc, which is attacked only with difficulty), 80 c.c. of hot dilute sulphuric acid (1 : 5) are run in and the whole heated to gentle ebullition, a funnel being placed in the neck of the flask to prevent loss by spurting. The molybdic acid, MoO_3, is reduced by hydrogen in stages which are indicated by a succession of colour changes—viz., rose, blue, green, brown and finally dark olive. The last substance formed has the uniform composition $Mo_{12}O_{19}$, although it probably consists of a mixture of several oxides. With a rapid evolution of hydrogen the reduction is complete in ten minutes. Any undissolved zinc is removed by filtration through glass wool, which is then rinsed with distilled water until the washings are colourless; the washings are added to the main bulk. The solution is titrated with standard permanganate until the dark colour is discharged and a faint rose tint is obtained. The lower oxides of molybdenum have now been reconverted into MoO_3.

Any error arising from the presence of traces of iron in the zinc is eliminated by dissolving the metal remaining on the filter-paper in sulphuric acid and titrating with permanganate; 10 grs. of the original zinc are titrated in the same way and a correction made for any iron titrated with the molybdenum.

The percentage of phosphorus is calculated in the following way: The yellow precipitate of ammonium phosphomolybdate has the composition $(NH_4)_3PO_4+12MoO_3$; therefore 1 atom of phosphorus corresponds to 12 molecules of MoO_3, which on reduction to $Mo_{12}O_{19}$ yields 17 atoms of oxygen. The same amount of oxygen is required in the subsequent titration with permanganate; hence 1 atom of phosphorus corresponds to 17 atoms of oxygen, or 1 c.c. of decinormal permanganate is equal to $\frac{31}{17\times2\times1000\times10}=0{\cdot}912\times10^{-4}$ grs. phosphorus.

As stated above, only a portion of the silica present in iron ores—viz., the uncombined silica—is reduced in the blast furnace, the remainder going into the slag. The phosphoric acid, however, is reduced completely and the whole of the phosphorus is taken up by the iron. The tenacity of iron is diminished by the presence of phosphorus, but its melting-point is lowered. For this latter reason, as also on account of its greater fluidity, iron containing phosphorus is generally used in the manufacture of ornamental castings.

3. Colorimetric Determination of Manganese.

This method is suitable only for samples of iron containing not more than about 1 per cent. of Mn, and cannot be used for spiegeleisen and ferromanganese, which should be analyzed by the method given under Iron Ores, (3), p. 141.

0·2 of the sample is heated in a 100 c.c. graduated flask with 15 to 20 c.c. of nitric acid (sp. gr. 1·2) until the evolution of red fumes ceases. The mixture is then allowed to cool and, without filtering, made up to the mark with water; 10 c.c. of the solution are pipetted into a small beaker, and boiled with about 2 c.c. of nitric acid (sp. gr. 1·2). A small quantity of lead peroxide, free from manganese, is then added, and the boiling is continued for two minutes. (The amount of lead oxide used should be such that only a very slight excess remains undissolved.)

The solution, which now contains the whole of the manganese as permanganic acid, is filtered through a wad of asbestos or glass wool into a graduated cylinder, like that used in the colorimetric estimation of carbon (p. 152), and the filter is washed with water until the washings are colourless. According to the hue of the solution, 1 to 4 c.c. of standard potassium permanganate containing 0·144 gr. $KMnO_4$ per litre are run into a similar test-glass and diluted until the tint corresponds to that of the sample; 1 c.c. of the permanganate solution is equivalent to 0·05 milligram of manganese.

If a c.c. represent the volume of the test solution, b c.c. that of the standard solution after dilution, and c c.c. that of the original standard solution taken for comparison, the amount of manganese in the standard permanganate is $c \times 0{\cdot}05$ milligram, and that in the 10 c.c. of iron solution taken for the test is

$$0{\cdot}05\, c \times \frac{a}{b} \text{ milligram Mn.}$$

Three or four tests should be made, using 10 c.c. of the iron solution in each case, and the mean of the results taken.

Manganese, in contrast to silicon, *prevents* the separation of graphite when cast iron solidifies, by promoting the formation of carbide. Hence molten manganiferous iron, on cooling, yields *white* cast iron. Manganese raises the melting-point and increases the hardness of the cast iron. A malleable steel containing a high percentage of manganese is manufactured under the name of " manganese steel "; this is extremely hard, but cannot be tempered in the ordinary sense of the word.

4. Determination of Sulphur.

The apparatus consists of a round-bottomed flask of about 600 c.c. capacity having a wide neck fitted with a cork. Three holes are bored in the cork. Through these pass respectively the stem of a dropping funnel, a small reflux condenser, and a bent tube which reaches nearly to the bottom of the flask and serves for the admission of gas.

5 grs. of cast iron (or 10 grs. of malleable iron) are placed in the flask and 50 to 100 c.c. of concentrated hydrochloric acid (sp. gr. 1·19) run in gradually from the dropping funnel. The hydrogen sulphide evolved is swept out of the apparatus by means of a slow current of carbon dioxide previously purified by washing with a solution of copper sulphate. The mixed gases pass out of the condenser into an Erlenmeyer flask containing about 100 c.c. of water, which serves to absorb any traces of hydrochloric acid carried over during the subsequent heating, and then through two smaller flasks in series, each containing 30 c.c. of 3 per cent. cadmium acetate solution, by which the whole of the sulphur is retained as cadmium sulphide.

When sufficient hydrochloric acid to dissolve the sample has been added and the evolution of hydrogen has practically ceased, the solution is gradually heated to boiling with the current of carbon dioxide still passing. After about five minutes' continuous boiling no hydrogen sulphide remains in the flask. The water in the wash-bottle is then boiled for a few minutes, after which the cadmium acetate flasks are detached and the contents rinsed into a beaker. By the addition of 6 to 10 c.c. of a 10 per cent. solution of copper sulphate acidified with sulphuric acid, copper sulphide is precipitated. The precipitate is filtered, and washed with hot water until the washings no longer give a coloration with aqueous hydrogen sulphide. The filter-paper and contents are then dried and ignited strongly in a crucible placed slantwise, to convert the copper sulphide into oxide. 79·6 grs. of copper oxide (CuO) correspond to 32 grs. of sulphur.

When iron is dissolved in highly concentrated hydrochloric acid, the sulphur is converted quantitatively into hydrogen sulphide. If dilute acid be used, small quantities of organic sulphides, such as methyl sulphide, $(CH_3)_2S$, are formed at the same time and are not retained by the cadmium acetate. The direct absorption of hydrogen sulphide in copper sulphate solution is impracticable, since any hydrogen phosphide present would cause the precipitation of metallic copper; cadmium solutions, however, are not decomposed by this gas. Instead of transforming the cadmium sulphide into copper sulphide, it may be titrated directly with iodine after acidifying with hydrochloric acid.

Sulphur is a highly objectionable impurity, whether in cast iron, in malleable iron, or in steel. If the furnace charge contains much lime or manganese, part of the sulphur passes into the slag as calcium sulphide or manganese sulphide, but the bulk of it goes into the iron.

Pig iron containing sulphur is unsuitable for casting or for the manufacture of steel. For the removal of sulphur, the molten metal is run into large "mixers," where it is mixed with manganiferous iron. After standing for some time, the greater portion of the sulphur separates on the surface as manganous sulphide. The presence of sulphur renders malleable iron brittle when hot ("red-short"); phosphorus, on the other hand, makes the iron "cold-short."

The following is a brief outline of the manufacture of the different kinds of iron:

(*a*) **Cast Iron.**—Since coke is always used in the reduction of iron ores, it is impossible to prevent the iron produced from absorbing carbon and other impurities (such as sulphur, silicon and phosphorus) from the ash and gangue; hence the first product obtained by direct smelting is always very impure.

The smelting operation takes place in the blast furnace, a vertical iron shaft 20 to 30 metres high lined with firebrick. Ore and coke in small lumps are charged alternately into the shaft through an opening at the top. The ore is previously mixed with the requisite amount of "flux," a material intended to unite with the gangue and ash to form an easily fusible slag. As most iron ores occur naturally with an acid gangue (silica), a basic flux is most generally used—viz., limestone or dolomite—which forms fusible calcium or magnesium silicates. If the gangue is basic, the flux employed must be acid. In this case argillaceous schist or other siliceous material is used. Whenever possible, two or more different ores with acid and basic gangues respectively are mixed together in the proportions necessary to form a suitable slag. Occasionally fluorspar is also added to increase the fluidity of the slag, but it is expensive and is also liable to attack the walls of the furnace. Where the furnace narrows towards the bottom (" boshes "), about 2 metres above the hearth, there are a number of water-cooled metal tubes (" twyers ") through which compressed air (" blast ") previously heated to 800°–900° C. is forced into the furnace.

The course of the reduction is as follows: At the point where the air enters, the coke burns to carbon dioxide, which, however, is quickly reduced to monoxide on coming into contact with the excess of coke in the next layer. The mixture of nitrogen and carbon monoxide, now at a temperature of about 2,000° C., ascends, heating and reducing the iron ore. Various zones of action are distinguished. In the upper part of the furnace the ore undergoes preliminary heating and dehydration (" heating zone "). Somewhat lower down, at a temperature of about 350° C., the reduction of the ore by the ascending carbon monoxide begins. At about 900° to 1,000° C. the reduction is almost finished, the iron then being in a solid spongy condition; the charge has now reached about the middle of the furnace, occupying the lower part of the " shaft " (" reducing zone "). On sinking still further, it encounters a rapidly increasing temperature. The iron is now taking up carbon from the fuel, as also phosphorus and silicon from the slag; some of the iron is absorbed in the slag, forming ferrous silicate, which, however, is reduced again at a higher temperature by the excess of carbon present. Finally the iron and slag are melted (" melting zone ") and drop into the bed of the furnace. The density of the slag is only about one-third that of the iron; hence it floats on the surface of the molten metal, protecting it from oxidation by the air blast. Immediately upon the hearth is a small opening plugged with a lump of fireclay, through which the iron can be tapped off. A second outlet, higher up, serves for the removal of the slag. The slag is run off periodically, after which the plug in the lower opening is pierced and the molten metal is allowed to flow into moulds of sand or cast iron, where it solidifies in the form of " pigs," or into a ladle for further treatment. Once started, a blast furnace may remain in continuous operation for several years.

In reducing the oxides of iron, carbon monoxide is itself oxidized to carbon dioxide. The waste gases leaving the furnace, however, always contain a considerable proportion of carbon monoxide. This is due to the fact that a state of equilibrium is established, and the reaction ceases when a certain proportion of carbon dioxide has been formed, which depends upon the temperature and upon the nature of the iron oxide involved.

The conditions of equilibrium between the oxides of carbon. metallic iron, and the oxides of iron, are represented by the following equations:

$$3Fe_2O_3 + CO \rightleftharpoons 2Fe_3O_4 + CO_2 \ldots\ldots\ldots (1).$$
$$Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2 \ldots\ldots\ldots\ldots (2).$$
$$FeO + CO \rightleftharpoons Fe + CO_2 \ldots\ldots\ldots\ldots\ldots (3).$$

In each of these equations there is a certain definite ratio between the amounts of CO_2 and CO, which depends upon the temperature, and is expressed, in accordance with the law of mass action, by

$$K = \frac{C_{(CO_2)}}{C_{(CO)}}.$$

For any given temperature the value of K is highest in equation (1) and lowest in equation (3)—*i.e.*, Fe_2O_3 is most easily reduced and FeO is least easily reduced, while Fe_3O_4 occupies an intermediate position.

But there also exists a state of equilibrium between CO_2, CO and the carbon of the fuel—

$$CO_2 + C \rightleftharpoons 2CO \ldots\ldots\ldots (4),$$

so that, according to the prevailing conditions, part of the carbon dioxide formed is reduced by the carbon (at high temperatures), or, conversely, some of the carbon monoxide present is converted into dioxide, with the separation of carbon (at low temperatures). In practice the waste gases contain about 26 per cent. CO, 13 per cent. CO_2 and 60 per cent. N, as also a small amount of hydrogen from the decomposition of the steam. They are utilized for preheating the air blast in huge regenerators (" Cowper stoves "), partly also for power to drive the blowers.

Either grey or white pig iron (p. 155) can be produced by modifying the furnace charge. The former is obtained by working with an acid slag containing free silica, the resulting metal containing silicon and graphite (*cf.* pp. 155 and 157); the product obtained in this way may be light grey, grey, or black pig iron, or finally ferrosilicon. Grey pig iron is used extensively for castings. White pig is obtained by keeping the slag basic and thus preventing silicon from entering into the iron. It is usual also to add manganese ore, so that a manganiferous iron free from graphite is produced (p. 159). The product is distinguished as ordinary white cast iron, white spiegel, spiegeleisen and ferromanganese, according to the amount of manganese present.

(*b*) **Malleable Iron (Wrought Iron and Steel).**—Malleable iron is always prepared from pig iron. The method consists essentially in removing as completely as possible all the impurities except carbon, a certain amount of which, varying from 0·05 to 1·6 per cent. according to requirements, is allowed to remain or is subsequently added. As the impurities are more easily oxidized than metallic iron, they can be removed by blowing a current of air through, or over the surface of, the molten metal. The sulphur is oxidized to SO_2, phosphorus to P_2O_5, silicon to SiO_2, manganese to its oxides, and the excess of carbon to CO_2. The most important methods for the production of malleable iron are:

(i.) *The Puddling Process.*—The cast iron is melted with iron slag in a reverberatory furnace lined with refractory iron oxides, and is stirred continually with long iron rods. The impurities are gradually oxidized by the lining material and the gases passing over the molten metal. Some of the iron is converted into Fe_3O_4, which on stirring into the mass also aids in the oxidation of the impurities. As the percentage of carbon diminishes, the melting-point of the iron is raised and the metal becomes increasingly viscous, until it can no longer be stirred. The pasty mass is kneaded for some time with an iron rod and then worked up into a number of separate lumps or balls, called "blooms." The balls are then pushed back into the hottest zone of the furnace, where the slag melts out, after which the glowing blooms are removed from the furnace, freed from adhering slag under a steam-hammer and while still red-hot rolled into bars. By this process iron containing about 0·1 per cent. of carbon is obtained. Fully 10 per cent. of the iron is lost as scale. The puddling process is now used only to a limited extent, having been superseded by the more rapid and less costly methods described below.

(ii.) *Bessemer Process.*—In the manufacture of steel by this process a "converter" made of wrought iron lined with siliceous material (Dinas rock) is employed. This is an egg-shaped vessel mounted on trunnions, so that it can be rotated round its horizontal axis ("Bessemer converter"). The converter is brought into a horizontal position and the charge of molten iron run in. It is then turned upright and a strong current of air, divided by numerous small holes at the base of the converter, is forced through the charge, whereby the silicon, manganese, and carbon are rapidly and completely oxidized. In this case the iron does not become pasty, as in the puddling process, because the temperature is raised above the melting-point of the decarbonized iron by the large amount of heat liberated in the combustion of the impurities, especially silicon. Iron containing phosphorus cannot be treated by the " acid " process, since the iron phosphate produced is decomposed by the silica of the lining material and the slag, liberating phosphoric acid, which is again reduced to phosphorus by the molten iron. For the preparation of steel from pig iron containing phosphorus the—

(iii.) *Thomas-Gilchrist or Basic Process* must be employed. In this the converter is lined with basic instead of acid material and basic slag is added during the blowing operation. The whole of the phosphorus then goes into the slag as calcium phosphate (see Basic Slag, p. 131).

Neither by the acid nor the basic process is it possible to produce in one operation iron containing the exact amount of carbon desired. It is necessary to oxidize the carbon almost completely, otherwise the phosphorus cannot be removed. The molten metal, which then contains some ferrous oxide, has to be recarbonized and deoxidized; this is done by adding the requisite amount of spiegeleisen containing a known amount of carbon or of ferromanganese. The manganese reacts with the ferrous oxide to form metallic iron and manganous oxide,

$$FeO + Mn = Fe + MnO,$$

the latter of which passes into the slag.

(iv.) *Siemens-Martin Process.*—Pig iron is melted with soft iron scrap low in carbon in proportions calculated to give a product containing an intermediate percentage of carbon—*i.e.*, steel. The process is conducted in a large reverberatory furnace having a trough-like hearth (Martin furnace). The high temperature required to melt the wrought iron is obtained by using the regenerative firing system introduced by Siemens. As in the puddling process, the impurities are removed by oxidizing with furnace gas. In this case, also, basic or acid furnace-linings and fluxes are employed according as the raw materials contain phosphorus or not.

(v.) *Annealing* (*Malleable Cast Iron*).—Small castings can be converted in the solid condition into malleable iron by embedding them in fine-grained red iron oxide and heating for twenty-four to thirty hours at 800° to 900° C. White pig iron alone is suitable for this purpose, since the carbon must be present in the combined form. During the heating, the combined carbon passes slowly to the outside and is oxidized by the ferric oxide. This method is used chiefly for the manufacture of small articles, such as keys, hooks and machine details.

(vi.) *Cementation.*—In this process, which may be regarded as the reverse of annealing, carbon is introduced into objects of wrought iron, such as scissors and knife-blades (*i.e.*, the exterior is converted into steel), by embedding them in wood charcoal and heating to about 1,000° C. for several days. The product so obtained is called " carburized steel " or " blister steel."

Steel produced by any of these methods always contains slag and gas cavities; to convert it into the finest tool steel further refining is required. For this purpose it is melted, with exclusion of air, in small fireclay crucibles of about 1 cwt. capacity, and maintained for a long period in the fluid condition, when the slag rises slowly to the surface and the small bubbles of gas escape. Steel refined in this way is known as " crucible steel." Of recent years the electric current has also been utilized in the refining of steel. In Héroult's furnace the current is supplied through a pair of carbon electrodes suspended just above the surface of the fused metal, arcing across the two intervening gaps. The metal is covered with a thick layer of molten slag to protect it from oxidation and prevent the absorption of carbon from the electrodes. In Kjellin's furnace the iron is melted by induction currents. The " electro-steel " obtained by either of these methods is in no way inferior to crucible steel.

19. ZINC BLENDE.

Determination of Zinc—(*a*) *Schaffner's Method.*—0·5 to 1 gr. of the finely powdered sample (according to the amount of zinc present) is heated in a beaker with 7 to 10 c.c. of concentrated hydrochloric acid until the odour of hydrogen sulphide is no longer perceptible. A few cubic centimetres of concentrated nitric acid are then added, and the heating continued until the evolution of nitric oxide has ceased. Finally, the solution is evaporated on a sand-bath with a small quantity of dilute sulphuric acid until white fumes appear, after which it is mixed with 50 c.c. of hot water and, without filtering, saturated with hydrogen sulphide.

The precipitate is removed by filtration and washed thoroughly with an aqueous solution of hydrogen sulphide slightly acidified with hydrochloric acid, the washings being added to the filtrate. After boiling well to expel all traces of hydrogen sulphide, the liquid is oxidized with bromine-water, again heated to boiling and mixed with a slight excess of ammonia. The precipitate is filtered off, redissolved in hot hydrochloric acid and, after adding a few drops of bromine-water, again thrown down with excess of ammonia. The filtrate, which contains the zinc, is collected in a thick-walled beaker, diluted with water to 500 c.c., and left standing for several hours (preferably overnight) to allow the excess of ammonia to escape.

Meanwhile a solution of zinc of known concentration is prepared by dissolving the chemically pure metal in hydrochloric acid. Several portions of this solution, each containing approximately the same amount of zinc as the sample under examination, are measured into beakers, made alkaline with ammonia, diluted to 500 c.c. with water, and set aside overnight. The solutions in the beakers are used to standardize a solution of sodium sulphide prepared by dissolving 40 grs. of the crystalline salt ($Na\ S.9H_2O$) in about

100 c.c. of water, filtering from any iron sulphide and diluting to 1 litre. On adding sodium sulphide to the ammoniacal zinc solution, zinc sulphide is precipitated. The end-point of the reaction is ascertained by putting a drop of the clear liquid on a sheet of glazed paper impregnated with lead carbonate, when a slight excess of the precipitant is detected by a faint brown coloration. The paper is exposed to the action of a drop of the liquid in every case for an equal time (ten to fifteen seconds), quickly rinsed with water and examined for the brown stain, which should be only just visible. The burette reading is taken and the end-point confirmed by adding a further 0·2 c.c. of the sodium sulphide solution and observing whether a more intense coloration is produced. The solutions of the sample are then titrated in exactly the same way. The sodium sulphide solution should be standardized just before use, as the titre is very liable to change.

Zinc ores are generally dissolved in aqua regia, but a better method is to remove the combined sulphur as far as possible in the form of hydrogen sulphide by treatment with hydrochloric acid. Any galena or copper pyrites present, which are not decomposed by hydrochloric acid, are then dissolved in aqua regia. The excess of nitric acid must be completely removed by evaporating with sulphuric acid, otherwise it would interfere with the subsequent titration by oxidizing the sodium sulphide. For this reason, also, any iron reduced by hydrogen sulphide during the precipitation of the metals of the second group is later oxidized with bromine, which also precipitates the manganese as dioxide. The excess of bromine is removed by boiling with ammonia,

$$3Br_2 + 8NH_3 = N_2 + 6NH_4Br.$$

(*b*) *Galetti-Fahlberg Method.*—The ore is treated exactly as described under (*a*) as far as the precipitation of the iron. The ammoniacal filtrate from the iron group is boiled in an Erlenmeyer flask until the bulk of the ammonia has been expelled. It is then mixed with 10 c.c. of dilute hydrochloric acid, diluted with water to 500 c.c., again heated to boiling and titrated hot with potassium ferrocyanide solution. The latter is prepared by dissolving 45 grs. of pure crystalline ferrocyanide, $K_4Fe(CN)_6.3H_2O$, in a litre of water. It is standardized against a solution of chemically pure zinc in dilute hydrochloric acid. A measured volume of the standard zinc chloride solution is carefully neutralized with ammonia, mixed with 10 c.c. of dilute hydrochloric acid, diluted to 500 c.c. with water, and heated to boiling. In titrating, the potassium ferrocyanide is added a few drops at a time to the hot solution of zinc chloride contained in an Erlenmeyer flask, which is well shaken. After waiting fifteen seconds for the precipitate to subside, a drop of the liquid is removed on the end of a glass rod and placed near a spot of 1 per cent. uranium acetate solution on a strip of filter-paper (free from iron), so that on spreading the two spots just touch. When a slight excess of ferrocyanide is present, a red stain is produced at the point of contact, which is seen distinctly on holding the paper up to the light. The observer should aim at securing the faintest visible tint. When the end-point appears to have been reached, the solution should be stirred thoroughly and again tested.

The precipitate obtained in the titration of zinc with potassium ferrocyanide is not pure zinc ferrocyanide, $Zn_2Fe(CN)_6$, but a compound having the approximate composition $K_2Zn_3[Fe(CN)_6]_2$, which, however, is uniform only if the titration is performed as described in a hot, slightly acid solution. Moreover, this substance is not formed instantaneously; hence the necessity of allowing the solution to stand after every addition of ferrocyanide.

Ferrocyanic acid forms with uranyl salts a brown precipitate (red in very dilute solution) of uranyl ferrocyanide according to the equation

$$2(UO_2)(NO_3)_2 + K_4Fe(CN)_6 = (UO_2)_2Fe(CN)_6 + 4KNO_3.$$

Zinc blende is the most important zinc ore employed for smelting. It is seldom found in the pure state, but is generally associated with iron pyrites, galena and occasionally copper pyrites. Frequently it also contains cadmium and traces of fluorides and mercury. This ore is widely distributed, extensive deposits occurring in Spain, France, Italy, Germany and especially in Algeria, Australia and North America.

Of the less important ores, mention may be made of *zinc spar* or calamine, $ZnCO_3$; *hemimorphite*, $ZnSiO_4.H_2O$; and *willemite*, Zn_2SiO_4 (anhydrous).

For the production of zinc the blende is first roasted, but this process is not so simple as in the case of iron pyrites (p. 76), where the mass, once ignited, continues to burn in a current of air. The heat of combustion of zinc blende is insufficient to maintain the required temperature without the aid of external heating. Moreover, during the roasting a considerable amount of zinc sulphate is formed, which is only decomposed at a very high temperature. The blende is roasted in muffles heated externally, through which the air required for oxidation is passed. The roast gases, which in this case are not contaminated with furnace gases, are suitable for the manufacture of sulphuric acid by the contact process (p. 87), owing to the fact that zinc blende generally contains less arsenic than pyritic ores. Some of the zinc blendes are quite free from arsenic.

The finely divided residue from the retorts (ZnO) is then mixed with coke dust and charged into long, narrow retorts made of fireclay (length about 5 feet, breadth about 1 foot). A large number (100 to 200) of these retorts are placed in a furnace horizontally in long rows, with several tiers arranged vertically one above the other, and heated by gas-firing to a white heat (1,110° to 1,300° C.). Only at this high temperature is the zinc oxide reduced by carbon; hence the zinc is liberated at a temperature well above its boiling-point (918° C.) and the metallic vapour passes out of the retorts together with the carbon monoxide:

$$\mathrm{ZnO} + \mathrm{C} = \mathrm{Zn} + \mathrm{CO}.$$

The metal is condensed and collected in the molten condition in small fireclay receivers, which are luted to the retorts and project only a little way out of the furnace, so that they are maintained at a temperature of about 450° C. The carbon monoxide escapes through a small hole in the receiver, carrying with it a small quantity of zinc vapour, which is condensed in metal cylinders (adapters) attached to the receivers. So long as any air remains in the adapters, some of the zinc burns to oxide, but once the air has been completely expelled by carbon monoxide, the metal, suddenly cooled below its melting-point (419° C.), is deposited in the form of very fine powder, the *zinc dust* of commerce.

The crude zinc obtained by the above process contains lead, a small amount of iron, and traces of silver, antimony, arsenic and cadmium. (The major portion of the cadmium, which is more easily reduced and has a lower boiling-point than zinc, escapes during the distillation and is partially condensed with the zinc dust.) The zinc is refined by remelting at the lowest possible temperature in the reducing atmosphere of a reverberatory furnace. The oxides rise to the surface and are skimmed off. At the low temperature employed, only about 1 per cent. of lead and 0·03 per cent. of iron alloy with the zinc, the rest collecting below the molten metal. The refined zinc now contains 98 to 99 per cent. Zn. It is only obtained free from lead by redistillation. For most purposes, however, this is not essential.

Zinc is largely employed in the form of sheets, which are made by rolling at a temperature of 120° to 140° C. At this temperature the metal is soft and ductile, while at ordinary temperatures it is inflexible and brittle. Large quantities of zinc are also used for galvanizing iron sheets and wire; this is done either by dipping the iron into molten zinc or by electrolytic deposition. Another important use of zinc is in the casting of ornaments.

The alloys of zinc are of great importance, especially brass (45 to 20 per cent. Zn, 55 to 80 per cent. Sn), red brass (Cu with less than 20 per cent. Zn) and the zinc bronzes.

20. ZINC DUST.

Determination of the Reducing Value.—0·5 gr. of the zinc dust, contained in a 250 c.c. measuring flask provided with a ground stopper, is shaken with 50 c.c. of a seminormal solution of potassium dichromate, 5 c.c. of a saturated solution of iron ammonium alum, and 5 c.c. of dilute sulphuric acid. After about five minutes a further 5 c.c. of dilute acid are added and the shaking continued for ten to fifteen minutes, when only a slight residue of silica should remain undissolved. The solution is diluted to the mark with water, and the excess of chromic acid in 50 c.c. determined by titration with decinormal ferrous ammonium sulphate previously standardized against potassium dichromate solution. (The latter is prepared from the pure salt dried at 130° C.) A measured volume of dichromate solution is acidified with dilute sulphuric acid and the solution of ferrous ammonium sulphate added a few drops at a time, whereupon the colour gradually changes from yellow to green. A drop of the liquid is removed and tested with a drop of *freshly prepared* dilute solution of pure potassium ferricyanide upon a strip of filter-paper free from iron (compare the titration of zinc, p. 169). A blue stain at the point of contact indicates a slight excess of ferrous salt.

Commercial zinc dust invariably contains a considerable amount of zinc oxide, together with small quantities of lead, arsenic, cadmium and iron. Since it is employed almost exclusively as a reducing agent, its value depends upon the amount of zinc present in the *metallic* condition. The reduction of potassium dichromate by zinc is represented by the equation

$$3Zn + K_2Cr_2O_7 + 7H_2SO_4 = 3ZnSO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

Any cadmium or iron present also takes part in the reduction, thus increasing the reducing value of the substance as determined by this method. The reaction between zinc and chromic acid is accelerated catalytically by the presence of salts of ferric iron.

A solution of neutral ferric sulphate or of alkaline potassium iodate may be used instead of chromic acid. Another method consists in dissolving the zinc dust in hydrochloric or sulphuric acids and measuring the volume of hydrogen evolved, or the hydrogen may be burnt with copper oxide and the water formed in the combustion absorbed and weighed.

The method described above yields sufficiently accurate results for ordinary purposes, while it is simple and expeditious.

21. GALENA.

Determination of Lead (Alexander-Sacher Method).—The sample is ground to extreme fineness and carefully sieved; 0·5 gr. (or 1 gr. if the ore contains less than 30 per cent. of lead) is dissolved in 10 to 15 c.c. of concentrated nitric acid in an Erlenmeyer flask. When the evolution of red fumes has ceased, 25 c.c. of dilute sulphuric acid are added, and the flask is heated on a sand-bath until thick white fumes appear. After allowing the mixture to cool somewhat, it is carefully diluted with 30 c.c. of hot water, and the heating continued for some time, with constant shaking. The contents of the flask are next cooled completely, and the solid matter—consisting of lead sulphate and gangue—is filtered off and washed with normal sulphuric acid. The filter containing the residue is transferred to a tall beaker of about 400 c.c. capacity (bearing on the outside a thin strip of label marking 250 c.c.) and heated with 25 c.c. of a faintly alkaline, concentrated solution of ammonium acetate and 100 c.c. of water until the lead sulphate is completely dissolved. The solution is slightly acidified with acetic acid, diluted to 250 c.c. with boiling water, and titrated immediately with ammonium molybdate solution.

The molybdate solution is prepared by dissolving 8·6 grs. of the chemically pure salt in water, adding a few drops of ammonia and diluting to 1 litre. A standard solution of lead is prepared by dissolving 16 grs. of pure lead nitrate (=10 grs. Pb) in a litre of water;* 50 c.c. of the lead nitrate solution, contained in a beaker similar to the above, are mixed with 25 c.c. of concentrated ammonium acetate, acidified slightly with acetic acid, diluted to 250 c.c. with boiling water and titrated as before with molybdate. A white precipitate of lead molybdate is produced. The end-point is ascertained by removing a drop of the clear liquid on a glass rod and testing it by the spot method with a freshly prepared 0·3 per cent. solution of tannic acid. The test is performed as described in the titration of zinc by the Galetti-Fahlberg method (p. 169). A drop of the liquid is placed upon a strip of filter-paper (free from iron) near a spot of partially dried tannic acid solution. A faint yellow stain at the point of contact indicates a slight excess of molybdate solution—*i.e.*, the precipitation of the lead is complete. Should the solution be overtitrated, it may be titrated back with standard lead nitrate; 0·7 c.c. should be deducted from the volume of ammonium molybdate used in the titration, this being the amount required, at the concentration employed, to produce a yellow coloration with a 0·3 per cent. solution of tannin. The latter solution, which does not keep well, is improved by the addition of 2 per cent. of acetic acid. If lead nitrate is not at hand, 10 grs. of pure lead foil may be dissolved in nitric acid, evaporated to dryness on a water-bath and dissolved in water to 1 litre; or a larger quantity of the salt may be prepared in this way and dried at 140° C. until constant in weight, 16 grams then being dissolved as before. The samples are titrated in exactly the same way. In this case also, 0·7 c.c. must be deducted from the volume of molybdate solution required.

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* An alternative method consists in dissolving 14·636 grs. of pure lead sulphate in ammonium acetate and diluting with water to 1,000 c.c.

Whereas molybdic acid forms with most bases a whole series of salts corresponding to polymolybdic acids of the general formula $n\text{MoO}_3.m\text{H}_2\text{O}$, only the metamolybdate of lead, PbMoO_4, is known. The titration method described above is based upon the fact that when a lead salt is added to an acetic acid solution of a soluble molybdate or polymolybdate, lead metamolybdate is precipitated quantitatively. The ammonium molybdate of commerce, $(\text{NH}_4)_6.\text{Mo}_7\text{O}_{24}.3\text{H}_2\text{O}$, is the salt of the polymolybdic acid, $\text{H}_6\text{Mo}_7\text{O}_{24}$ $(=7\text{MoO}_3.3\text{H}_2\text{O})$. The nature of the reaction between this salt and tannin, in presence of acetic acid, is obscure.

Galena or *lead glance*, PbS, is the most widely distributed and important ore employed in lead-smelting. It invariably contains a small amount of the isomorphous *silver glance*, Ag_2S and is generally associated with zinc blende, pyrites, chalcopyrite and mispickel.

Other less important ores of lead are *cerussite,* or white lead ore, $PbCO_3$, which occurs especially at Broken Hill, in New South Wales; *anglesite,* or lead vitriol, $PbSO_4$; and the brown *pyromorphite,* $3Pb_3(PO_4)_2.PbCl_2$, sometimes found on galena.

Three principal methods are employed for the production of metallic lead:

(*a*) *Precipitation Process.*—The galena is decomposed by heating with iron ($PbS + Fe = FeS + Pb$). This process is only applicable to ores containing very little arsenic and antimony. It is conducted in a lead blast furnace, the charge consisting of a mixture of galena and iron oxide with coke as fuel. The reaction indicated in the above equation is always incomplete, since a part of the galena melts up with the iron sulphide produced, forming a "matte" ($PbS + FeS$), from which the lead can only be recovered by further treatment.

(*b*) *Roast and Reaction Process.*—The finely crushed ore is roasted at a moderate temperature in a reverberatory furnace with admission of air, by which a part of the lead sulphide is converted into oxide and sulphate, while about one-third of the ore remains unaltered. The temperature is then raised, and the charge, which begins to soften, is stirred to promote the interaction of the oxidized material with unchanged sulphide. The following reactions take place:

$$2PbO + PbS = SO_2 + 3Pb.$$
$$PbSO_4 + PbS = 2SO_2 + 2Pb.$$

The molten metal thus produced is run into a receiver. Fine coal or charcoal is then stirred into the mass to reduce the excess of oxide and a further quantity of lead is drawn off. For this process rich ores containing at least 65 to 70 per cent. of lead are required; they should not contain any appreciable quantity of siliceous matter, otherwise fusible lead silicate is formed, which glazes over the particles of ore and thus hinders the roasting.

(*c*) *Roast and Reduction Process.*—This process is the most generally employed, as it is suitable for all kinds of ore. Low-grade ores are first concentrated to about 60 per cent. of lead by dressing. The ores are then roasted as completely as possible, generally in reverberatory furnaces, but sometimes in shaft furnaces. If the ore contains copper, a corresponding amount of sulphur is left in the roasted material, to form matte (Cu_2S) during the subsequent reducing operation. In the more recent process of Huntingdon and Heberlein, the galena is mixed with lime and roasted in a reverberatory furnace until one-half of the sulphur has been removed. The fine-grained material is then transferred to a converter and blown with a current of air, whereupon the charge melts and the sulphur is expelled almost completely as sulphur dioxide. The following reactions are supposed to take place:

$$CaO + PbS = CaS + PbO.$$
$$CaS + 2O_2 = CaSO_4.$$
$$CaSO_4 + PbO = SO_2 + CaPbO_3 \text{ (calcium plumbate).}$$

The roasted material obtained by either of these methods, consisting chiefly of lead oxide, is then reduced with coke in a shaft furnace. If any considerable quantity of lead silicate be present, iron oxide is added; these substances react readily, with the formation of lead oxide and iron silicate.

The metallic lead liberated by reduction collects at the bottom of the furnace and is tapped off. Any lead matte or lead copper matte formed floats above the liquid metal, and is itself covered by a layer of molten slag.

The crude metal thus obtained is then submitted to some process of refining, according to the nature and amount of the impurities present. The recovery of gold and silver is particularly important.

22. OILS, FATS, AND WAXES.

The natural animal and vegetable fats are divided into three classes: (1) Solid fats or tallows; (2) liquid fats or oils (also called "fatty oils," to distinguish them from mineral oils, which consist of hydrocarbons); and (3) waxes.

The methods of investigation applied to these substances are identical. A complete analysis—*i.e.*, a quantitative determination of all the constituents—is not only impracticable, owing to their highly complex character, but also unnecessary for ordinary commercial purposes. The main objects of the analysis are to identify a particular fat and to ascertain whether the sample is adulterated with other fats.

The composition of any fat in its natural state is generally uniform; hence, as a rule, the sample can be identified with a fair degree of certainty by means of a few preliminary qualitative tests, but more particularly by the quantitative determination of the so-called "constants"* of the fat. The adulteration of any particular sample is detected by the deviation of the found values from the normal "constants."

A baffling problem in fat analysis is the identification of the individual components of a mixture of fatty substances.

The scheme of analysis presented here is restricted to the determination of the most important "constants." For a more elaborate examination the student should consult a special textbook on this subject.

As far as edible fats are concerned, chemical and physical tests, which, as already stated, are only intended to establish the identity of a sample and its freedom from adulteration, are not in themselves conclusive. The goodness of an edible fat depends mainly upon its appearance, odour and, above all, palatableness; the estimation of its value from these properties calls for long practical experience and a cultivated sense of taste.

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* Lewkowitsch recommends the use of the term *characteristics* in place of *constants*, "to indicate the fact that, although the numbers are specific for each kind of fat or wax, they still allow of certain fluctuations within narrow limits" ("Chemical Technology and Analysis of Oils, Fats, and Waxes," 5th ed., 1913, p. 378.—*Tr.*).

The methods of examination are physical and chemical.

The physical methods are limited to the following determinations:

(1) Specific gravity.
(2) Melting-point and freezing-point.
(3) Refractive index.
(4) Viscosity.
(5) Optical activity.
(6) Solubility.

Important information is obtained from (1), (2), and (3). For the determination of the viscosity see p. 211. The optical activity of a fat is very small, but it is useful in detecting adulteration with resin, since the latter possesses a high rotatory power.

The chemical examination consists of a few preliminary qualitative tests, followed by quantitative determinations. Of the former, the elaïdin test and the oxygen-absorption test may be mentioned, both of which serve to distinguish drying from non-drying oils.

Certain oils possess the property of absorbing considerable quantities of oxygen from the air and drying to a varnish. The mechanism of this oxidation process has not been satisfactorily explained. The test consists in exposing a thin smear of the oil on a glass plate to the air for several days.

Well-known drying oils are those of linseed, poppy, and hemp.

The elaïdin test is based upon the fact that liquid ole c acid and its glyceride are converted by nitrous acid into solid isomeric elaïdic acid (or solid elaïdic ester). This test is applied in the following way: 10 grs. of the oil are shaken in a test-tube with about 3 c.c. of concentrated nitric acid and 1 drop of mercury for a few minutes; the mercury dissolves, reducing the nitric to nitrous acid. The mixture is then allowed to stand for twenty-four hours, when the non-drying oils containing oleïn (*e.g.*, olive, almond, castor and many other oils) solidify partially or completely, while the drying oils remain unchanged.

Quantitative Determinations.

1. Sampling.—Liquid fats, if not perfectly clear, are first passed through a dry filter. Solid fats are melted in a small dish on the water-bath and the clarified molten fat is decanted from any sediment or water through a dry filter, which removes the last traces of moisture.

2. Saponification Value.—The saponification value (Koettstorfer number) represents the number of milligrams of potassium hydroxide required to saponify 1 gram of the fat.

1·5 to 2 grs. of the purified fat or oil are weighed into a flask of about 200 c.c. capacity and 25 c.c. of an alcoholic solution of potassium hydroxide are added from a pipette. The flask is connected to a reflux condenser, and the mixture boiled for thirty minutes on the water-bath with occasional shaking. When saponification is complete the liquid should be quite homogeneous; no drop of oil should remain either at the bottom of the flask or floating on the surface. If too much alcohol has been lost during the heating, it is replaced by the addition of *pure* alcohol. The alkali remaining in the solution is then titrated with seminormal hydrochloric acid, using phenolphthaleïn as indicator. A blank experiment is made with 25 c.c. of alcoholic potash in exactly the same way. The difference between the volumes of hydrochloric acid required in the two titrations corresponds to the amount of alkali used in the saponification.

The potash solution is prepared by dissolving about 30 grs. of caustic potash ("pure by alcohol") in the smallest possible quantity of water and making up to a litre with 96 per cent. alcohol. The solution is allowed to stand for some time and if not perfectly clear it is passed through a large folded filter. The stock-bottle is preferably closed with a rubber stopper. The solution is standardized against seminormal hydrochloric acid.

Example: 1·5243 grs. of olive oil are saponified with 25 c.c. of alcoholic potash, corresponding to 25·3 c.c. of seminormal hydrochloric acid. After the saponification 14·9 c.c. of the same acid are required to neutralize the excess of potash. The amount of potash consumed is therefore equivalent to $25{\cdot}3 - 14{\cdot}9 = 10{\cdot}4$ c.c. of seminormal HCl $= 10{\cdot}4 \times 28$ mgrs. KOH; or 1 gr. of the oil requires

$$\frac{10{\cdot}4 \times 28}{1{\cdot}5243} = 191 \text{ mgrs. KOH.}$$

The saponification value is thus 191.

Fats and waxes are composed of the esters of fatty acids, together with minute traces of free fatty acids (see under Acid Value, p. 194). On adding alkali, the free acids are neutralized and the esters are then saponified—*i.e.*, split up into alcohols and the metallic salt of the fatty acid; hence the saponification value represents the neutralization equivalent of all the acids present in the fat or wax.

The alcohol residue of the fatty esters consists almost entirely of the trivalent alcohol *glycerol*, $C_3H_5(OH)_3$, with which the fatty acids are combined in the form of triglycerides, $C_3H_5(R.COO)_3$.

A very large number of natural fats are composed chiefly of the triglycerides of *palmitic acid*, $C_{15}H_{31}.COOH$; *stearic acid* $C_{17}H_{35}.COOH$; and *oleïc acid*, $C_{17}H_{33}.COOH$. The molecular weights of these three acids, hence also their neutralization equivalents, are approximately the same.

Theoretically, 1 gr. of pure tripalmitin, $C_3H_5(C_{15}H_{31}COO)_3$, requires for its saponification 208·4 mgrs. of KOH; pure tristearin, $C_3H_5(C_{17}H_{35}COO)_3$, 188·8 mgrs. KOH; and pure trioleïn, $C_3H_5(C_{17}H_{33}COO)_3$, 190 mgrs. KOH; hence the saponification values of the majority of fats lie between 190 and 200.

Should any given sample have a saponification value differing greatly from the normal, it may be assumed to be one of a very limited number of fats. Further, it is obvious that the lower the molecular weight of the acid, the higher its saponification value must be and *vice versa*. Thus, butter fats, palm-kernel oil and coconut oil, have abnormally high saponification values, because they contain acids of low molecular weight, such as *butyric acid*, $C_3H_7.COOH$; *caproic acid*, $C_5H_{11}.COOH$; *caprylic acid*, $C_7H_{15}.COOH$; *capric acid*, $C_9H_{19}.COOH$; *lauric acid*, $C_{11}H_{23}.COOH$. Conversely, the oils of the rape-seed (colza) group have abnormally low saponification values, owing to the presence of *erucic acid*, $C_{21}H_{41}.COOH$, which has a very high molecular weight. The members of the castor-oil group, on account of the oxyacids which they contain, have low saponification values.

The waxes do not contain glycerides, but are composed of the esters of monovalent alcohols of high molecular weight, such as *cetyl alcohol*, $C_{16}H_{33}.OH$; *octodecyl alcohol*, $C_{18}H_{37}.OH$; and *myricyl* alcohol, $C_{30}H_{61}.OH$. The latter, for instance, occurs in beeswax. Some animal waxes contain the aromatic alcohols *cholesterol* and *isocholesterol* (*cf.* p. 195), wool wax, for example, being composed almost entirely of the esters of these two alcohols

The alcohol radicles of waxes have higher molecular weights than those of fats, while the acid radicles are usually common to both; for this reason the saponification values of the waxes are consistently lower than those of the fats, lying, as a rule, between 80 and 135.

The determination of the saponification value thus offers a simple means of distinguishing waxes from fats and oils.

The average saponification values of the most important fats and waxes are given below.

A.—Fats.

(1) *Normal Saponification Values.*

Beef tallow	190 to 200
Mutton tallow	
Lard	
Goose fat	
Olive oil	
Cotton-seed oil	
Linseed oil	
Poppy-seed oil	

(2) *High Saponification Values.*

Coconut oil	246 to 260
Palm-kernel oil	242 to 250
Butter	221 to 233

(3) *Low Saponification Values.*

Castor oil	183 to 186
Rape oil	170 to 179

B.—Waxes.

Wool wax	102
Flax wax	102
Beeswax	90 to 98
Carnaüba wax	79 to 95

3. Determination of the Reichert-Meissl Value.—The Reichert-Meissl value represents the number of cubic centimetres of decinormal caustic potash required to neutralize the volatile fatty acids contained in 5 grs. of the fat.

5 grs. of the purified fat are weighed into a 200 c.c. flask, mixed with 2 grs. of solid caustic potash and 50 c.c. of 70 per cent. alcohol and heated on a water-bath with constant agitation until the alcohol has evaporated completely. The residual soap is then dissolved in 100 c.c. of water and the solution mixed with 40 c.c. of dilute sulphuric acid (1: 10). The flask is connected through a bent tube, with a large bulb blown on it, to a sloping water-cooled condenser (Fig. 33), and the mixture distilled. The distillate is collected in a graduated receiver. The rate of distillation is carefully controlled, so that 110 c.c. pass over in as nearly as possible one hour. 100 c.c. of the distillate, passed through a dry filter, are titrated with decinormal caustic potash, using phenolphthaleïn as indicator. The number of cubic centimetres of alkali required, multiplied by 1·1, gives the Reichert-Meissl value.

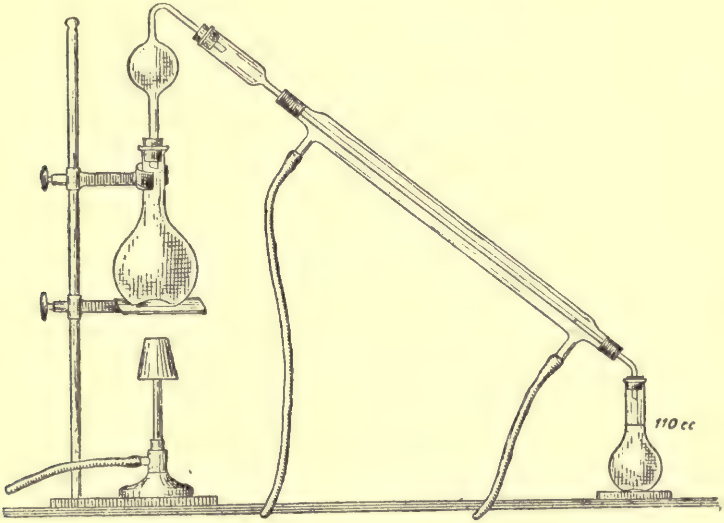


Fig. 33.

The amount of volatile fatty acids present in the majority of natural oils, fats, and waxes is very small; hence the Reichert-Meissl value is usually less than 1·0. Higher values are obtained only from a very limited number of fats, the presence of which is thus disclosed by this method. Dolphin oil and porpoise oil contain an exceptionally high percentage of volatile fatty acids, especially *valeric acid,* $C_4H_9.COOH$. Butter, and to a less extent palm-kernel oil and coconut oil, are also characterized by a high content of volatile acids.

Table of Reichert-Meissl Values.

Beef tallow	0·0
Mutton tallow	
Lard	
Rape oil	
Poppy-seed oil	
Cotton-seed oil	
And many others	
Olive oil	0·6
Palm-kernel oil	5 to 6
Coconut oil	7 to 8·5
Flax wax	9·3
Butter fat	27 to 30

4. Determination of the Hehner Value.—The Hehner value represents the percentage of fatty acids insoluble in water, in an oil or fat.

3 to 4 grs. of the fat are saponified as described in the preceding determination and the alcohol evaporated. The soap paste is dissolved in water, acidified with sulphuric acid, and heated until the liberated fatty acids float on the top as a clear oil. The contents of the flask are then passed through a filter-paper previously weighed in a large, stoppered bottle after drying at 100° C. Before the filtration the filter should be wetted with hot water and it should be kept full throughout the operation. The fatty acids on the filter are washed with a large volume of boiling water until a few cubic centimetres of the washings show complete neutrality to litmus *solution*. The filter is then transferred to the weighing-bottle and dried at 100° C. for three hours. The increase in weight, calculated for 100 grs. of the sample used, gives the Hehner value.

The average molecular weight of the isolated fatty acids is then determined. For this purpose the filter containing the residue is treated in a flask with 50 c.c. of neutral alcohol-ether mixture (1 : 2) with which the weighing bottle has previously been rinsed out. The solution is titrated with alcoholic potash, as described under Acid Value (p. 194).

Since the acids in question are all monobasic, 1,000 c.c. of normal alkali solution neutralize exactly an average gram-molecule of fatty acid. For example, if a c.c. of normal alkali are required to neutralize n grs. of fatty acid, the mean molecular weight of the latter is given by

$$M = \frac{1000 \times n}{a}.$$

Strictly speaking, the Hehner value does not give the percentage of fatty acids alone, but that of the fatty acids *plus* unsaponifiable matter, since under the above treatment these substances separate out together. The amount of unsaponifiable matter in oils and fats is for the most part negligibly small, but in waxes it often equals, and sometimes even exceeds, that of the fatty acids. For this reason the determination of the Hehner value is useless in the case of waxes.

The Hehner values of most of the fats and oils lie between 95 and 96. Only in a few cases are water-soluble fatty acids present and even in these the percentage does not vary greatly, since, as already stated, the molecular weights of the acids commonly present in fats and oils are very similar. Theoretically, tristearin contains 95·7 per cent., tripalmitin 95·3 per cent., and trioleïn 95·7 per cent., of the respective fatty acids. When water-soluble fatty acids are present the Hehner value found is less than the mean value given above. Now, the only fatty acids soluble in water are those which have low molecular weights. It has already been observed (p. 181) that the latter have high saponification values. As a rule they are also volatile in steam. We can thus understand why fats and oils which have exceptionally high saponification values usually have high Reichert-Meissl values, but low Hehner values. This is strikingly illustrated by the examples of dolphin oil and porpoise oil (which substances, however, are rarely encountered in commerce). The "constants" of these oils are:

	Saponification Value.	*Reichert-Meissl Value.*	*Hehner Value.*
Dolphin oil (jaw) ..	290	65·9	66·3
Porpoise oil (jaw) ..	254 to 272	47·8 to 65·8	70·2

The most important Hehner values for other fats and oils are:

Beef tallow Mutton tallow Lard Rape oil Poppy-seed oil Cotton-seed oil Sesamé oil	95·0 to 96·0
Palm-kernel oil	87·6 to 91·1
Coconut oil	88·6 to 90·0
Butter fat	86·5 to 90·0

In the following tables are given the molecular weights of the fatty acids *insoluble* in water which commonly occur in fats and oils, as also the *average* molecular weights of the mixture of fatty acids obtained from a number of the natural fats by neutralization:

(*a*) Molecular weights of fatty acids—

Palmitic acid, $C_{15}H_{31}.COOH = 256$
Stearic ,, $C_{17}H_{35}.COOH = 284$
Oleïc ,, $C\ H_{33}.COOH = 282$
Linolic ,, $C_{17}H_{31}.COOH = 280$
Linolenic ,, $C_{17}H_{29}.COOH = 278$
Ricinoleïc ,, $C_{17}H_{32}(OH).COOH = 298$
Arachidic ,, $C_{19}H_{39}.COOH = 312$
Erucic ,, $C_{21}H_{41}.COOH = 338$

(*b*) Mean molecular weights of fatty acids from—

Linseed oil	285
Cotton-seed oil	277 to 270
Sesamé oil	280
Rape oil	303
Olive oil	291
Castor oil	292
Cod-liver oil	275 to 271
Palm-kernel oil	217 to 212
Coconut oil	217 to 211
Lard	278
Beef tallow	284
Butter fat	267 to 255

5. Determination of the Iodine Value.—The iodine value represents in terms of iodine the percentage of iodine chloride absorbed by a fat or wax.

(*a*) *Hübl's Method.*—0·15 to 1·0 gr. of the sample, contained in a 500 c.c. bottle provided with a well-ground stopper, is dissolved in 10 c.c. of chloroform or carbon tetrachloride and mixed with 25 c.c. of iodine chloride run in from a pipette. The stopper is immediately inserted and the bottle shaken vigorously. The solution should be clear and homogeneous, otherwise more chloroform must be added, after which it is allowed to stand in the dark for twelve to eighteen hours. Should the deep brown colour of the solution disappear after a few hours, a further 25 c.c. of iodine solution must be added.

A blank experiment with the chloroform and iodine solutions is made in the same way.

When the absorption is complete, 20 c.c. of a 10 per cent. solution of potassium iodide are added and the mixture diluted with 300 c.c. of water. Should any mercuric iodide be precipitated, it is dissolved by the addition of more potassium iodide. The free iodine is then titrated with decinormal sodium thiosulphate. During the titration the bottle is shaken frequently. The iodine gradually passes from the chloroform into aqueous solution. When both layers exhibit only a faint coloration, a few drops of freshly prepared starch solution are added and the titration continued until the blue colour is discharged. (The colour which generally reappears on prolonged standing may be disregarded.) The blank experiment is similarly performed.

The iodine chloride reagent is prepared in the following way: 25 grs. of iodine and 30 grs. of mercuric chloride are each dissolved separately in 500 c.c. of 95 per cent. alcohol. The latter solution, if not perfectly clear, should be filtered. Equal volumes of these solutions are then mixed together and allowed to stand for twenty-four hours before use, since the titre at first changes considerably. As the mixture does not keep well, the solutions should preferably be stored in separate bottles and mixed as required.

Method of Calculation.—0·5524 gr. of mutton tallow is mixed with 25 c.c. of the iodine solution, corresponding to

56·7 c.c. of decinormal thiosulphate solution. On titrating the excess of iodine, 38·4 c.c. of thiosulphate are required. Now, 56·7 − 38·4 = 18·3 c.c. of *decinormal* iodine solution, or 18·3 × 0·0127 gr. of iodine have been consumed. Hence 100 grs. of the fat would require $\frac{0{\cdot}2324 \times 100}{0{\cdot}5524} = 42{\cdot}07$ grs. I_2.

The iodine value is thus 42·07.

For the standardization of thiosulphate pure potassium dichromate is used, which, if necessary, should be recrystallized from hot water. It is dried at 120° to 130° C. for thirty minutes, after which 4·903 grs. are dissolved and made up with water to 1 litre; 20 to 25 c.c. of dichromate solution are transferred to a 600 to 800 c.c. stoppered bottle, mixed with 10 c.c. of a 10 per cent. solution of potassium iodide (free from iodine) and 30 to 40 c.c. of dilute hydrochloric acid, and allowed to stand for fifteen minutes. The solution is then diluted with 500 to 600 c.c. of water, after which the free iodine is titrated in the usual way with thiosulphate, using freshly prepared starch solution as indicator. The object of allowing the mixed solutions of dichromate and iodide to stand is to secure the complete reduction of the chromic acid by hydriodic acid—a reaction which is by no means instantaneous. The higher the concentration of the solution, the more rapidly does the reduction proceed; for this reason the water is not added immediately.

Pure iodine in solution is but slowly absorbed by the fatty acids and the results obtained by its use are variable. A mixture of iodine and chlorine, however, is rapidly and regularly absorbed.

When alcoholic solutions of mercuric chloride and iodine are mixed together, a partial interaction takes place, according to the equation

$$HgCl_2 + 2I_2 \rightleftharpoons HgI_2 + 2ICl.$$

The amount of iodine chloride formed is small, but as fast as this is absorbed by the fat a further quantity is produced. The alteration in the titre of the standard solution is due to the hydrolysis of iodine chloride by the water contained in the alcohol:

$$ICl + H_2O \rightleftharpoons HCl + HIO.$$

The hypoiodous acid produced oxidizes a small amount of alcohol to aldehyde, with the simultaneous formation of water,

$$C_2H_5.OH + 2HIO = CH_3.CHO + I_2 + 2H_2O,$$

which brings about further hydrolysis, and so on. By the addition of excess of hydrochloric acid to the original mixture of mercuric chloride and iodine, the formation of hypoiodous acid is retarded and the keeping qualities of the solution are thus improved.

The following modification of the above method is frequently employed:

(*b*) *Wijs' Method.*—7 to 8 grs. of iodine trichloride (ICl_3) and 8·5 grs. of iodine are dissolved separately in glacial acetic acid on the water-bath, care being taken that the acid does not absorb moisture during the operation. The solutions are then mixed together in a litre flask and made up to the mark with glacial acetic acid. According to Lewkowitsch, the solution can be conveniently prepared by dissolving 13 grs. of iodine in a litre of pure glacial acetic acid and, after determining the titre, passing a current of pure, dry chlorine through the solution until the original titre is exactly doubled. This point is indicated by a distinct change of colour when all the iodine has been converted into iodine monochloride. The method is then identical with that of Hübl, except that the fat is dissolved in carbon tetrachloride, because commercial chloroform frequently contains alcohol. In this case it is not necessary to prolong the treatment with iodine chloride, as in Hübl's method. When the iodine value of the fat is below 100, the reaction is complete in half an hour; when it exceeds this value, one hour or at most two hours is sufficient. The glacial acetic acid and carbon tetrachloride used should be quite free from oxidizable substances. They are tested by adding a small quantity of potassium dichromate and sulphuric acid (with heating in the case of acetic acid). No green coloration should appear even after long standing. Since the titre of the solution keeps very constant, a blank test with every analysis is unnecessary.

When iodine is added to iodine trichloride, the monochloride is formed—

$$ICl_3 + I_2 = 3ICl.$$

The rapid action of Wijs' solution is due to the high concentration of iodine chloride employed.

In the titration of iodine chloride with thiosulphate an equivalent of iodine is titrated in place of chlorine, since the potassium iodide added to the solution is decomposed, with liberation of iodine—

$$ICl + KI = KCl + I_2.$$

The iodine value of a fat corresponds to the amount of unsaturated acids, or rather to the esters of unsaturated acids, present. The latter absorb halogens and are converted into saturated halogen compounds. Thus trioleïn is converted into di-halogen-tristearin, according to the equation

$$C_3H_5(C_{17}H_{33}COO)_3 + 3ICl = C_3H_5(C_{17}H_{33}IClCOO)_3.$$

The unsaturated acids represented in the form of their esters in fats belong to several different series:

(i.) *Acrylic or Oleïc Acid Series,* $C_nH_{2n-1}.COOH$.—These compounds absorb two atoms of halogen. The most important member of this series is *oleïc acid,* $C_{17}H_{33}.COOH$, to which frequent reference has been made. It occurs in the majority of vegetable and animal fats. Another member, which has a low molecular weight, is *tiglic acid,* $C_4H_7.COOH$, found in croton oil. *Eruric acid,* $C_{21}H_{41}.COOH$, occurs in rape oil.

(ii.) *Linolic Acid Series,* $C_nH_{2n-3}.COOH$.—The acids of this series absorb four halogen atoms. A good example is *linolic acid,* $C_{17}H_{31}.COOH$, which occurs, together with a number of its isomers, chiefly in the drying oils, but also to a limited extent in the non-drying oils.

(iii.) *Linolenic Acid Series,* $C_nH_{2n-5}.COOH$.—These acids absorb six halogen atoms. The most important is *linolenic acid* itself, $C_{17}H_{29}.COOH$, which is characteristic of the strong drying oils, and predominates in linseed oil.

(iv.) *Isanic Acid Series,* $C_nH_{2n-7}.COOH$.—These absorb eight halogen atoms. Of this series two acids are known —viz., *isanic acid,* $C_{13}H_{19}.COOH$, found in certain seeds; and *therapic acid,* $C_{16}H_{25}.COOH$, the chief constituent of cod-liver oil.

The iodine-absorption value is the most useful of the "constants" employed in fat analysis, since it offers the readiest means of determining the group to which a particular oil belongs.

The highest iodine numbers are possessed by the drying oils, followed by those of the non-drying oils and fats. All the waxes have low iodine values.

Table of the Most Important Iodine Values.

(1) Drying Oils.	
Linseed oil	171 to 201
Hemp-seed oil	148
Poppy-seed oil	133 to 143
Cod-liver oil	154 to 181
(2) Semi-drying Oils.	
Cotton-seed oil	106 to 110
Rape oil	94 to 102
(3) Non-drying Oils.	
Olive oil	79 to 88
Castor oil	83 to 86
Palm-kernel oil	13 to 14
Coconut oil	8 to 9·5
(4) Fats.	
Goose fat	67 to 71
Lard	50 to 70
Beef tallow	38 to 46
Mutton tallow	35 to 46
Butter	26 to 38
(5) Waxes.	
Wool wax	17 to 29
Carnaüba wax	13·5
Beeswax	8 to 11
Insect wax	1·4

6. Determination of the Acetyl Value (Benedikt-Lewkowitsch).—The acetyl value represents the number of milligrams of potassium hydroxide required to neutralize the acetic acid obtained on saponifying 1 gram of an acetylated fat or wax.

10 grs. of the sample are heated with 20 grs. of acetic anhydride for two hours in a round-bottomed flask fitted with a vertical condenser *ground* into the neck. The solution is poured into a large beaker, mixed with 500 c.c. of boiling water and heated for thirty minutes with a slow current of carbon dioxide passing through the liquid to pre-

vent bumping. On standing, the liquid separates into two layers. The aqueous layer is siphoned off and the acetylated oil is washed with 500 c.c. of boiling water as before. This treatment is repeated once more, after which the washings should no longer show an acid reaction with litmus. The washing operation must not be unnecessarily prolonged, otherwise the substance may undergo slight decomposition. The acetylated product is then filtered through a *dry* filter and dried in the oven.

5 grs. of the acetylated oil are saponified by boiling with alcoholic potash, as described under Saponification Value (p. 180); the alcohol is evaporated over the water-bath, and the soap dissolved in warm water. A quantity of seminormal sulphuric acid, slightly in excess of that corresponding to the potash used, is then added, and the mixture heated gently until the fatty acids have collected on the top as an oily layer. The free fatty acids are filtered off and washed with boiling water until the washings no longer give an acid reaction; the filtrate is then titrated with decinormal alkali, using phenolphthaleïn as indicator.

Method of Calculation.—10 grs. of castor oil are acetylated, and 4·7321 grs. of the product saponified with 75 c.c. of alcoholic potash, corresponding to 76·4 c.c. of seminormal sulphuric acid. After adding 80 c.c. of seminormal sulphuric acid and filtering off the fatty acids, 149 c.c. of decinormal caustic potash are required to neutralize the filtrate.

The excess of sulphuric acid added corresponds to $80 - 76{\cdot}4 = 3{\cdot}6$ c.c. of seminormal, or 18 c.c. of decinormal, potash; therefore $149 - 18 = 131$ c.c. of the latter have been consumed in neutralizing the acetic acid liberated, or 1 gr of the acetylated oil requires $\frac{131 \times 5{\cdot}6}{4{\cdot}7321} = 155{\cdot}2$ mgrs. KOH.

The acetyl value of the castor oil is thus 155·2.

When a fat is boiled with acetic anhydride, the hydroxyl groups are replaced by acetyl groups.

The reactions which take place in the acetylation of castor oil, for example, may be represented as follows:

$$\underset{\text{Ricinoleïn.}}{2C_3H_5[C_{17}H_{32}(OH)COO]_3} + 3(CH_3CO)_2O = \underset{\text{Acetyl ricinoleïn.}}{2C_3H_5[C_{17}H_{32}(OCH_3CO)COO]_3} + 3H_2O.$$

The acetylated product, on boiling with alkali, is saponified again—*i.e.*, the acetyl group is split off as acetic acid. Since the fatty acids liberated from the glycerides during the saponification have been removed by filtration, the acidity remaining after the potash has been neutralized by an equivalent amount of sulphuric acid is due to the acetic acid set free.

In fresh oils the hydroxyl groups are present exclusively in the form of esters of hydroxy acids. These occur notably in castor oil, but also to a less extent in other oils and in waxes. The chief constituent of castor oil is the ester of the unsaturated *ricinoleïc acid,* $C_{17}H_{32}.OH.COOH$. Among the saturated hydroxy acids may be mentioned the monohydroxy compounds *lanopalmic acid,* $C_{15}H_{30}.OH.COOH$, in wool wax, and an acid having the composition $C_{20}H_{40}.OH.COOH$ in carnaüba wax; of the dihydroxy acids the most important are *dioxystearic acid,* $C_{17}H_{33}(OH)_2\,COOH$, which also is present in castor oil to the extent of about 1 per cent., and *lanoceric acid,* $C_{29}H_{57}(OH)_2.COOH$, found in wool wax.

In the method of determining the acetyl value originally introduced by Benedikt, not the fats themselves, but the acids obtained from them by saponification, were acetylated. Lewkowitsch, however, showed that the free higher fatty acids, on boiling with acetic anhydride, are partially converted into anhydrides, with the simultaneous formation of acetic acid:

$$2C_{15}H_{31}.COOH + (CH_3CO)_2O = (C_{15}H_{31}CO)_2O + 2CH_3.COOH.$$

Since the anhydrides of the higher fatty acids are very stable, resisting the action of boiling water, and not being completely hydrated by alkali, the acetyl values found by Benedikt's method are too high.

In regard to his own method, also, Lewkowitsch has pointed out that the real acetyl value (*i.e.*, that derived from the substitution of the -OH group in hydroxy acids by an acetyl group) is only obtained when triglycerides alone are present. While the *fresh* natural oils and fats contain triglycerides exclusively, stale oils and fats may contain, in addition, di- and monoglycerides formed by spontaneous hydrolysis according to the equations

$$C_3H_5(RCOO)_3 + H_2O = C_3H_5(OH)(RCOO)_2 + RCOOH,$$

and

$$C_3H_5(RCOO)_3 + 2H_2O = C_3H_5(OH)_2(RCOO) + 2RCOOH.$$

Since the hydroxyl groups formed in this way are also replaceable by acetyl groups, the values found after treating the stale fats with acetic anhydride are too high.

The acetyl value may thus be taken as a constant only in cases where it is certain that triglycerides alone are present, as, for example, in castor oil and the waxes, which are only hydrolyzed with difficulty. In the case of other oils the acetyl value, taken in conjunction with the acid value (*vide infra*), gives some indication of the staleness and rancidity.

The acetyl value of most fats and oils is very small, only castor oil and the waxes having high values.

Acetyl Values.

Castor oil	153 to 156	
Carnaüba wax	55	
Wool wax	23	
Beeswax	15	
Rape oil	about 14	variable.
Olive oil	about 10	
Linseed oil	about 4	
Lard	about 2·6	

7. Determination of the Acid Value.—The acid value represents the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in 1 gram of a fat or wax.

5 to 10 grs. of the fat or wax are dissolved in pure alcohol, or a mixture of pure alcohol and pure ether, and titrated with decinormal alkali, using phenolphthaleïn as indicator. The end-point is reached when the red coloration persists for several seconds.

Example: 7·32 grs. of a fat require 4·2 c.c. of decinormal caustic potash for neutralization. The acid value is

$$\frac{4\cdot2\times5\cdot6}{7\cdot32}=3\cdot21.$$

The percentage of free acid in oil or wax is not uniform, but depends upon the purity and freshness of the sample, as also on the amount of hydrolysis which may have taken place. Fresh animal fats are practically neutral, while many vegetable fats in the natural state contain a small amount of free acid. Although the acid value is not a constant, it affords a useful indication of the quality of the sample examined. In general, a good oil or fat should possess a low acid value apart from the fact that a maximum permissible acidity is usually fixed. Other important determinations are the following:

8. Determination of Glycerol.—20 grs. of the fat are saponified with alcoholic potash, as described on p. 180. After the alcohol has been expelled by heating on a water-bath, the soap is dissolved in water and treated by the method given on p. 204.

9. Determination of Unsaponifiable Matter (Allen and Thomson's Method).—10 grs. of the fat are saponified by heating on the water-bath with 50 c.c. of alcoholic caustic soda (80 grs. NaOH in 1,000 c.c. of alcohol), the flask being shaken continually until a lather is just produced; 15 c.c. of alcohol are then added and 5 grs. of sodium bicarbonate stirred in (to convert the excess of sodium hydroxide into carbonate), followed by 50 to 70 grs. of fine sand, previously ignited. The mass is dried at 90° C. for twenty minutes, and then extracted with petroleum ether in a Soxhlet apparatus.

Finally, the solvent is evaporated and the residue weighed. The petroleum ether should not contain any fraction boiling over 80° C., otherwise it must be submitted to a preliminary distillation.

As already stated (p. 182), the waxes are not glycerides, but esters of monovalent alcohols of high molecular weight. Many of them—*e.g.*, beeswax—also contain small quantities of free hydrocarbons of high molecular weight. When a wax is saponified, the hydrocarbons and alcohols (which, unlike glycerol, are insoluble in water) separate out with the free fatty acids. On extracting the dried soap mixture with petroleum ether, the alcohols pass into solution, while the salts of the fatty acids remain behind with the glycerol.

Generally speaking, the unsaponifiable matter comprises all those neutral substances which are insoluble in water and do not react with caustic soda to form soaps, but are soluble in ether and petroleum ether. The pure natural fats and oils contain only minute quantities of these substances, but the form in which they occur is characteristic. Thus all animal fats are distinguished by the presence of unsaponifiable *cholesterol*, while vegetable fats, without exception, contain traces of unsaponifiable *phytosterol*. Both of these are monovalent alcohols having the empirical formula $C_{26}H_{43}.OH$. (The occurrence of cholesterol and the isomeric isocholesterol in waxes, especially in wool wax, has already been mentioned.) Since these alcohols can readily be distinguished by their crystalline forms, melting-points, and more particularly by the melting-points of their acetates, this test is of great value in detecting the adulteration of animal fats with vegetable fats (*e.g.*, the addition of coconut fat to butter).

The following table gives the percentages of unsaponifiable matter generally found in pure natural fats and waxes:

	Per cent.
Linseed oil	0·4 to 1·1
Olive oil	0·5 to 1·0
Castor oil	0·3
Cod-liver oil	0·5 to 7·8
Lard	0·35
Carnaüba wax	55·0
Wool wax	43 to 52
Beeswax	52 to 55

If the amount of unsaponifiable matter found in a fat or oil considerably exceeds the above average, adulteration with solid or liquid unsaponifiable substances, such as paraffin, ceresin, mineral oils, resin oils, or tar oils, may be inferred. The particular adulterant is identified by a special examination.

Oils and fats are mainly used as foods, but large quantities are utilized in the industries as lubricants and illuminants, as also for the manufacture of soap, candles and varnishes. Vegetable oils and fats are obtained either by expression or by extraction with volatile solvents. While a moderate pressure is sufficient to express the oil from fruits such as the olive, that from seeds and kernels is only recovered by using extremely high pressures. The seeds are ground to a coarse powder, packed in cloths, and submitted to a pressure of upwards of 200 atmospheres in hydraulic presses. For the recovery of superior edible oils, the material is first pressed cold. A second and third compression at a higher temperature yield oils of inferior appearance and taste which are only fit for industrial purposes. The residue from the compression, called "oil-cake," still contains 8 to 15 per cent. of oil and is a valuable feeding-stuff for cattle.

The method of extraction by solvents is limited in its application by the fact that the oils thus obtained are unfit for food. The solvents most commonly used are petroleum ether and carbon disulphide. Carbon tetrachloride, CCl_4, is an excellent solvent which possesses the advantage of being non-inflammable, but it is too expensive for general use.

Two processes of extraction are employed: (1) The crushed seeds are leached on the counter-current principle in closed iron vessels and the saturated solution distilled to recover the solvent; or (2) a limited quantity of the solvent is used in a continuous apparatus resembling the laboratory Soxhlet extractor. In both cases the product generally needs refining.

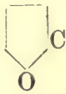
Oils obtained by expression are usually turbid owing to the presence of cellular tissue and mucilage, either in suspension or solution; they are clarified by passing through a filter-press. Free fatty acids are removed by treatment with alkali. The colour of dark edible oils is improved by filtration through animal charcoal. Industrial oils are bleached with pyrolusite and sulphuric acid, bleaching powder, or a mixture of potassium dichromate with hydrochloric acid, and finally purified with superheated steam.

The most important edible oils are the following:

Olive oil, obtained from the fruit of the olive, chiefly in Italy, is the most valuable table oil.

Earth-nut oil (arachis oil) is obtained in Africa, India and North America from earth-nuts (pea-nuts).

Poppy-seed oil and *beech-nut oil* are mostly indigenous products.

Sesamé oil is prepared in large quantities in Germany from the seeds of the sesamé plant, imported from India. It is distinguished from all other fats by a very characteristic colour test which is performed in the following manner: To a few drops of a 2 per cent. alcoholic solution of furfurol,  CHO, in a test-tube, add 10 c.c. of the oil, followed by 10 c.c. of concentrated hydrochloric acid, and shake vigorously. The presence of as little as 1 per cent. of sesamé oil produces a deep red coloration.

In Germany all margarine must contain 10 per cent. of sesamé oil, in order that it may be readily distinguished from natural butter by this sensitive reaction.

Cotton-seed Oil.—The extraction of this oil has developed into an extensive industry in the U.S.A. since a method was discovered of preparing a good edible product from the dark-coloured and unpalatable crude oil by treatment with caustic soda.

The chief solid vegetable fats used in commerce, mainly as butter substitutes, are *coconut fat*, obtained from the kernels of the coconut, *palm-kernel fat*, and *cocoa-butter*.

Animal fats are obtained by melting down the crude fats, generally by means of steam. Solvents are rarely employed, a notable exception being the extraction of *bone fat.* By far the most important edible animal fat is *butter,* now recovered on a large scale in central dairies by means of centrifugal machines which separate the whole milk into cream and skim milk. Commercial butter consists of 80 to 85 per cent. of butter fat together with 15 to 20 per cent. of skim milk—*i.e.,* water containing small quantities of casein, milk sugar, lactic acid and mineral matter. Pure butter fat is obtained from butter by heating the latter at 50° C. until the upper oily layer is perfectly clear. This is removed by skimming, and dried in an oven. Lard, beef tallow and mutton tallow are extracted by rendering at the lowest temperature. *Lard* is a superior edible fat. *Beef tallow* is generally not used alone, but mixed with lard or other fat. It can be separated by expression at 35° C. into a hard portion consisting chiefly of tristearin, called *press tallow,* and a softer portion containing more tripalmitin and particularly trioleïn, known as oleomargarine. The latter is used for the preparation of margarine. For this purpose a quantity of oleomargarine mixed with a certain proportion of lard and vegetable fat is heated to melting, and emulsified with skim milk at a temperature of 27° to 29° C. to a homogeneous mass which, after kneading and pressing out the excess of milk, closely resembles natural butter in appearance and taste. A large number of other oils besides the inferior qualities of those already mentioned are employed in the industries, particularly for the manufacture of soap and candles. Their importance as burning oils has declined since the introduction of mineral oils. (See also under Lubricants).

The drying oils, of which *linseed oil* is the most important, are also employed for various purposes. Linseed oil is obtained by expression from the seeds of the flax plant, which is extensively cultivated for this purpose in Russia (whence the best qualities are obtained), as also in India and North America. The drying of linseed oil by absorption of atmospheric oxygen is accelerated in an extraordinary degree by the addition of small quantities of salts of manganese or lead. By melting the fatty acids of linseed oil or resins with lead oxide, or by treating sodium linoleate or sodium resinate with manganous sulphate, substances known as *siccatives* are obtained, which are the metallic salts of linolic or resinic acids. When a small quantity of these salts is stirred into linseed oil heated to 120° to 150° C., a varnish is obtained which, after working up with a pigment, is extensively used as paint. By dissolving melted resins such as copal and amber (colophony is not so good) in linseed oil and mixing the solution with turpentine, the so-called colourless *lacquers—e.g.*, copal varnish and amber varnish—are produced, which on triturating with pigments yield *enamels*.

For the preparation of printer's ink, linseed oil is thickened by boiling and mixed with lamp black.

Linseed oil is also used in the preparation of linoleum. The oil, after being resinified by submitting it to a current of air, is melted with colophony and worked up while still hot with powdered cork.

Waxes are usually extracted by hand. The most important are the following:

Beeswax is the material of which the honeycombs are constructed. The combs, from which the honey has been removed by centrifuging, are repeatedly melted and pressed out under water. The crude yellow wax is rolled into thin strips, exposed to sunlight and sprinkled frequently with water, when it is gradually bleached perfectly white, like linen treated in the same way. Beeswax is a valuable material for the making of candles; it is also largely used in furniture and floor polishes.

Carnaüba wax is extracted from the leaves of a South American palm. The leaves are dried in the sun, the white powder brushed off and melted into lumps under water. This vegetable wax, like beeswax, is made up into candles.

Wool fat is obtained from "wool-scourer's suds," the waste water from wool-washing, or is extracted from the fleece with petroleum ether. It possesses the property of forming with water an emulsion which has the appearance of a homogeneous substance. An emulsion of this kind is sold as a cosmetic under the name of "lanoline."

Sperm oil is a liquid wax contained in the head cavity of the sperm whale. Owing to the fact that it has little tendency to become rancid, it is used extensively as a lubricant for spindles and fine machine bearings.

23. SOAP.

SOAP dries on exposure to the air, a hard skin being formed on the exterior, which thus contains less water than the average of the whole cake. Hence, in the case of hard soaps, the sample should be taken from the centre of the piece, while for soft soaps the exposed outer layer is scraped away and the sample taken from beneath.

The weighing should be done as rapidly as possible. Soaps containing much water are best weighed in a stoppered bottle or in a beaker covered with a watch-glass.

1. Determination of Fat and Total Alkali.—5 to 10 grs. of the sample are weighed into a beaker and dissolved in hot water, the solution being stirred with a glass rod to prevent the soap from sticking to the walls of the vessel. A few drops of methyl orange, followed by a measured excess of normal sulphuric acid, are added and the solution heated with constant stirring until the fatty acids have separated on the surface as a clear oily layer; 5 grs. of dry paraffin wax are then stirred in, the glass rod is rinsed with boiling water, and the heating continued until the two layers have again separated completely. Upon cooling, the fatty layer solidifies. By means of a thin spatula the solid cake is detached and lifted out of the beaker; it is then rinsed with cold water and dried with filter-paper. Any residue of fat still adhering to the walls of the beaker is scraped off and added to the bulk. If the cake contains liquid inclusions, it should be melted over hot water, again allowed to solidify and treated as before. The fat thus freed from water is placed in a tared watch-glass, dried thoroughly in a desiccator and weighed. After deducting the weight of the paraffin, the remainder is calculated to fatty anhydride. In making the calculation, the mean molecular weight of the fatty acids is taken at 275; hence for every 275 grs. of fat found, $\frac{1}{2}$ molecule or

9 grs. of water must be subtracted; or the weight of the fat may be multiplied by the factor 0·9673.

The acidic liquor is filtered and the excess of acid titrated with normal caustic soda. From the amount of sulphuric acid consumed, the total alkali, which is expressed as Na_2O in hard soaps and as K_2O in soft soaps, is calculated.

The object of adding paraffin is to obtain the fatty acids in a hard cake, thus facilitating their separation from the liquor. Many soaps, especially those prepared from coconut oil and palm-kernel oil, contain considerable quantities of water-soluble fatty acids. In such cases concentrated solutions should be employed for the analysis, or the liquor should be saturated with common salt, thereby reducing the solubility of the fatty acids to a negligible quantity. In exact analysis the purity of the separated mass should be tested. The fatty acids may contain resin, neutral fat, and unsaponifiable matter.

Common resin, or *colophony,* is the residue obtained after distilling crude pine resin until the turpentine and moisture have been expelled. Resin, on heating with dilute alkalis, dissolves, forming salts or resin soaps, which in some respects resemble soaps prepared from fats and oils—viz., they are hydrolyzed by water and on agitation produce a lather. For this reason the resinic acids are reckoned as equivalent to fatty acids, and are generally reported as such in an analysis.

The separated fatty acids should be tested quantitatively for resin by the *Liebermann-Storch reaction:* 1 to 2 c.c. of the liquefied fatty acid are dissolved in acetic anhydride, $(CH_3CO)_2O$, by heating gently in a test-tube. After cooling, a drop of sulphuric acid (sp. gr. 1·53), prepared by mixing equal parts by volume of concentrated sulphuric acid and water, is added. The presence of resin acids is indicated by a reddish-violet coloration, which rapidly disappears. Should a quantitative determination of the resin acids be necessary, it is best made by *Twitchell's method,* in which the separation is effected by esterifying the fatty acids. When an alcoholic solution of fatty acids is treated with gaseous hydrochloric acid, the fatty acids are converted quantitatively into their ethyl esters, while the resin acids under the same treatment remain practically unchanged. Devine recommends the following procedure: About 3 grs. of the mixed acids are weighed into a dry flask and dissolved in 25 c.c. of *absolute* alcohol. The solution is well cooled by immersing the flask in cold water and then mixed with 25 c.c.

of absolute alcohol previously saturated with dry hydrochloric acid gas. (The latter is most conveniently prepared by dropping fuming hydrochloric acid into concentrated sulphuric acid.) After standing for twenty minutes, 10 grs. of dry granulated zinc chloride are added, the mixture is again cooled and set aside for twenty minutes. It is then diluted to about 200 c.c. with water and the alcohol expelled by boiling. The solution, after cooling, is transferred to a separating funnel and shaken with ether (previously used to rinse the flask), by which the resin acids, together with the ethyl esters of the fatty acids, are extracted. The acidic aqueous layer is run off and the ethereal solution washed with water until it is quite free from hydrochloric acid. The ether is then evaporated, the residue dissolved in pure alcohol and titrated with decinormal caustic soda, using phenolphthaleïn as indicator. The resin acids alone take part in the titration, the ethyl esters remaining unchanged. The combining weight of resin is taken as 346; hence 1 c.c. of decinormal caustic soda corresponds to 0·0346 gr. of resin.

Neutral fat—*i.e.*, unsaponified fat—is rarely found in soaps, with the exception of the so-called "superfatted" soaps, to which olive oil or some similar oil has been added after the saponification.

Unsaponifiable matter includes all those neutral substances soluble in ether and petroleum ether, originally derived from the fats or oils used in the preparation of the soap, together with those which may have been intentionally added. All natural fats contain a small amount of unsaponifiable matter (*cf.* p. 195). Among the common unsaponifiable adulterants are paraffin wax, vaseline, petroleum hydrocarbons and naphthalene.

For the determination of neutral fats and unsaponifiable matter, the free fatty acids must first be converted into their alkali salts, which are *insoluble* in ether; the neutral fats and unsaponifiable matter are then extracted with ether and weighed together, after evaporating the solvent. Finally, the residual mixture is boiled with alcoholic potash to saponify the neutral fats, evaporated to dryness and again shaken with ether, whereby the unsaponifiable matter alone is extracted.

2. Determination of Free Alkali, Combined Alkali, Free Fatty Acids, and Substances Insoluble in Alcohol.—10 to 30 grs. of soap are placed in a filter-cartridge previously weighed after drying at 100° C. and extracted with absolute alcohol in a Soxhlet apparatus. Soaps containing much moisture should first be partially dehydrated by heating gradually to 60° C. and finally for a few minutes at 90° to 100° C., care being taken to protect them from carbon dioxide.

When the extraction is complete, a few drops of phenolphthaleïn are added to the solution. Should a red coloration be produced, indicating the presence of free alkali, the solution is titrated with decinormal hydrochloric acid. If, on the other hand, an acid reaction is given, free fatty acids are present, and the solution must be titrated with decinormal caustic soda.

The residual solution from the titration is diluted with water. Owing to the hydrolysis of the soap, a red coloration is produced, which, however, may be disregarded. Methyl orange is added, and the alkali salt of the fatty acids titrated with normal hydrochloric acid.

Free alkali is expressed as NaOH (or KOH). The average molecular weight of the free fatty acids is taken as 275; hence 1 c.c. of decinormal caustic soda corresponds to 0·0275 gr. of fatty acids. Finally, the combined alkali must be calculated to Na_2O (or K_2O), since the combined fatty acids in (1) are expressed as anhydrides.

The insoluble matter left after extraction with alcohol is dried at 100° C. and weighed. Good soaps leave only a slight residue; if any considerable quantity remains, it should be submitted to further examination. If the amount of *total alkali* found in (1) exceeds that of the free caustic alkali (expressed as Na_2O) *plus* the alkali combined with the fatty acids, the difference is due to "feebly combined" alkali insoluble in alcohol—*i.e.*, alkali combined with weak acids and not indicated by methyl orange. This may be present as sodium silicate, carbonate, or borate. The residue is extracted with hot water and the filtrate treated with hydrochloric acid; the presence of carbonates is indicated by an effervescence, that of water-glass by the separation of flocculent silica. Boric acid is detected in the usual way by the alcohol-sulphuric acid test. The residue insoluble in water is ignited to destroy any organic matter and tested qualitatively by the ordinary methods.

Free alkali is almost invariably present in soft soaps, but superior household soaps, especially toilet soaps, should not contain more than the merest trace, since it has an irritating action on the skin, is injurious to textile fabrics (particularly woollen goods) and destroys or alters the colour of dyes. Free fatty acids likewise should be absent. Their presence might be due to the addition of an excess of these substances in neutralizing the free alkali during the process of manufacture, or to the neutral fats in the finished soap subsequently becoming rancid. The best soaps are perfectly neutral. In addition to borax, water-glass and soda, the residue insoluble in alcohol may contain a number of other substances, such as starch, lime, barytes, chalk, sand, common salt and sodium sulphate. With the exception of borax and water-glass, which also possess detergent properties, these substances are to be regarded as adulterants or fillers. As much as 25 per cent. of sugar was formerly found in the cheapest transparent soaps. It may be determined by extracting the residue insoluble in alcohol with water, hydrolyzing with dilute sulphuric acid, adding excess of caustic soda, and heating with Fehling's solution in the usual way. Larger amounts of sugar can also be determined by means of a polarimeter. Starch is best detected by its reaction with iodine. For the quantitative determination the insoluble residue, after extracting the sugar with cold water, is boiled with dilute sulphuric acid, whereby the starch is converted into glucose, which may then be estimated with Fehling's solution.

3. Determination of Glycerol.—10 to 30 grs. of soap are dissolved in water, and the fatty acids removed by treating with dilute sulphuric acid as described under (1). The aqueous solution is filtered, neutralized with barium carbonate and evaporated to the consistency of syrup. This is extracted with a mixture of 95 per cent. alcohol and ether in the proportion of 3 : 1, filtered, evaporated on the water-bath to a small bulk and dried in a desiccator. The crude glycerin thus obtained is then treated by the acetin method (p. 209).

Soft soaps and semi-boiled soaps, which cannot be separated from the lye, contain the whole of the glycerin liberated in the saponification, but the amount of glycerin present in hard soaps prepared by the boiling process is so small that a large quantity of the sample must be taken for an accurate determination. In the preparation of many toilet soaps a considerable quantity of glycerin is added to the soap in the milling machine, and constitutes a valuable ingredient.

4. Determination of Water.—For most purposes it is sufficient to estimate the amount of water by difference. If a direct determination is required, one of the following methods may be used:

(*a*) About 5 grs. of the soap in the form of thin shavings are dried at 70° C. for one hour, and then at 100° C. until constant in weight; the hard crust forming on the slices is occasionally pierced with a thin platinum wire to facilitate the drying. If the soap contains free alkali, the shavings are weighed in a stoppered U-tube through which a current of air, free from moisture and carbon dioxide, is passed during the drying operation. This operation requires several hours.

A more rapid method is the following:

(*b*) *Fahrion's Method.*—A quantity of oleïc acid free from volatile matter is prepared by heating oleïn for a few minutes at about 120° C. It is preserved in a well-stoppered bottle; 2·5 to 4 grs. of the soap are weighed into an open crucible, mixed with about three times its weight of the prepared oleïc acid, and again weighed. The crucible is then heated gently over a small flame until the water has been completely expelled and the soap dissolves in the oleïc acid, forming a clear solution. A slight turbidity, due to the presence of inorganic " fillers," is readily distinguished from that caused by water. The contents of the crucible must not be heated so strongly as to produce an odour of burning, otherwise the result will be too high. At least two determinations, which ought to agree to within ½ per cent., should be made.

The amount of water in soaps is extremely variable. Fresh, undried soap contains at least 30 per cent., but this is greatly reduced in the preparation of good hard toilet soaps. Conversely, by the addition of " filling " substances, such as waterglass, sodium carbonate and sulphate, the water content can be enormously increased without the soap becoming too soft. Examples of such " filled " or " weighted " soaps are the very cheap domestic varieties, which frequently contain not more than 15 to 20 per cent. of true soap, the rest consisting of water and other substances.

The term " soap " properly refers to the alkali salts of the higher fatty acids. Soaps are prepared from fats and fatty oils, the raw materials of manufacture including vegetable and animal fats of the most varied descriptions. Two methods of converting the fats into soaps are in use. The older method, which is still most generally employed, consists in heating the fat with caustic lyes, whereby the alkali salts of the fatty acids are formed and glycerin is liberated. In the newer process the fat is first decomposed without the use of alkali, the glycerin removed and the pure free fatty acids then converted into soap by neutralizing with alkali. In the first case caustic alkali is required for the saponification, but in the latter the neutralization can be effected with alkali carbonates.

When sodium is used for the saponification or neutralization, the hard *sodium soaps* are obtained, whereas potassium under the same conditions yields soft *potash soaps*, the "soft soaps" of commerce. There are, however, different degrees of hardness, owing to the fact that soap is not a uniform substance, but consists of a mixture of salts of different fatty acids, which vary with the raw materials employed in its manufacture.

Of the three most important salts, sodium stearate and palmitate are much harder than sodium oleate; hence a sodium soap prepared, for example, from tallow—a fat very rich in stearin—is necessarily harder than one obtained from olive oil, rich in oleïn. Moreover, the hardness of a soap also depends upon the amount of water contained in it, and the filling substances added.

In the direct saponification of fats, the raw material, contained in an iron vessel, is emulsified by blowing in steam, and the requisite amount of caustic soda solution is added in portions at gradually decreasing intervals. A slight excess of alkali is required to decompose the glycerides completely. During the process of saponification the fats dissolve in the lye, forming a homogeneous product consisting of soap liquor, glycerin and some free caustic soda. From this solution the soap is obtained by "salting out." Ground rock salt is stirred into the boiling liquor until, on standing, a separation into two layers takes place, the soap curd floating upon the aqueous solution of salt, glycerin and excess of caustic soda. The lower layer is drawn off. The soap curd is then redissolved in very weak caustic soda, a small quantity of salt added, and the soap boiled on the lye until the curd forms a homogeneous mass. It is then allowed to stand for a few hours until the mother-liquor has separated, when the viscous soap is filled into frames, where it remains for several days until completely solidified. The soap mass thus obtained contains 30 to 35 per cent. of water; occasionally the water content is increased by stirring hot water into the clear-boiled soaps (" settled soaps ").

For the production of *toilet soaps* the curd, which in this case should be prepared from the best materials, is shredded, dehydrated to about 6 to 8 per cent. water, coloured and perfumed. It is then kneaded together until uniformly mixed and compressed in a "plodding" machine, from which it issues in the form of a continuous bar. This is cut into cakes, which are then shaped in the stamping press.

If, instead of salting out the curd after saponification, the whole mass is allowed to solidify, *semi-boiled soaps* are obtained which contain the whole of the glycerin and the excess of alkali.

When caustic potash is used for the saponification, pasty *soft soaps* are obtained. These can be prepared only in the gelatinous form, since on adding common salt interaction takes place, with the formation of sodium soap and potassium chloride. As a rule, the soft soaps contain much water; a large amount of potassium carbonate is often added as a " filler." On account of their solubility, the soft soaps are largely employed for domestic and industrial purposes.

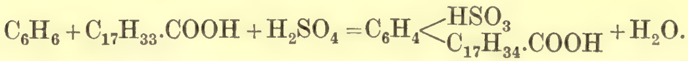
In preparing soaps from free fatty acids, the latter are melted and neutralized with a solution of sodium carbonate. Carbon dioxide is evolved. Any fat present must be saponified by subsequent boiling with caustic soda. The soap paste obtained in this way is treated as before.

The following are the most important methods of obtaining free fatty acids from fats:

(1) *Saponification in Autoclaves.*—While fats heated under pressure with water alone are not split up below about 200° C., at which temperature a large proportion of the organic matter is destroyed, the addition of a small quantity of a base, such as lime, magnesia, or zinc oxide, brings about the decomposition at 150° to 160° C. In practice zinc oxide is commonly employed; 0·5 per cent. of this substance mixed with an equal amount of zinc dust is added to the emulsion of fat and water. Under a pressure of 6 atmospheres saponification is complete in about eight hours. The fatty acids are separated from the specifically heavier layer of aqueous glycerin, stirred with sulphuric acid to decompose the zinc soap formed, washed with water and then

either worked up directly into soap or first distilled *in vacuo* or with superheated steam.

(2) *Saponification by Twitchell's Method.*—When fats are treated with sulphuric acid at 100° C., the unsaturated acids which they contain are converted into sulphonic acids. If the reaction is interrupted before charring takes place, the excess of free sulphuric acid removed and the mixture boiled with water under atmospheric pressure, a complete saponification of the fats is produced by the catalytic action of the sulphonic acids. The objections to this method in practice are that a certain amount of charring and consequent discoloration of the fats is unavoidable, while the unstable sulphonic acids are gradually hydrolyzed on boiling, forming sulphuric acid, by which a considerable amount of the glycerin is destroyed. For this reason Twitchell, instead of adding sulphuric acid directly to the fats, uses a specially prepared sulphonic fatty acid, or rather one of the aromatic sulphonic fatty acids (which is much more stable than the first named, besides being a more active catalyst)—*e.g.*, benzo-sulpho-stearic acid prepared by the interaction of benzene, oleïc acid and sulphuric acid, thus:



$$C_6H_6 + C_{17}H_{33}.COOH + H_2SO_4 = C_6H_4{<}\begin{matrix}HSO_3\\ C_{17}H_{34}.COOH\end{matrix} + H_2O.$$

According to the nature of the fat employed, 0·3 to 3 per cent. of this reagent is added and the mass boiled without interruption for twelve to fourteen hours. The free fatty acids are then separated from the sulphonic acids by washing with water and treating as in the autoclave process.

(3) *Saponification with Ferments.*—Of recent years fat-splitting enzymes such as *lipase* have been employed. This enzyme is obtained from the seed of the castor-oil plant. The seed is ground up with water and the "milk" so obtained allowed to ferment spontaneously; a thick cream containing the ferment separates on the surface and is skimmed off. The fat is mixed with 30 to 40 per cent. of water and 4 to 10 per cent. of the ferment emulsion is added, together with a small quantity of a neutral salt, usually manganous sulphate, as "activator"; 85 to 90 per cent. of the fat is saponified in about forty-eight hours; the mass separates into two layers, the fatty matter on the top and aqueous glycerin below.

24. GLYCERIN.

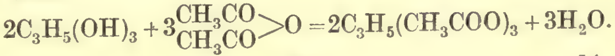
A.—Crude Glycerin.

1. Determination of Glycerol.—1 to 2 grs. of crude glycerin are placed in a round-bottomed flask of about 100 c.c. capacity, with a reflux condenser *ground* into the neck, and heated for one and a half hours with 8 to 10 c.c. of acetic anhydride and 4 grs. of anhydrous sodium acetate. After allowing the mixture to cool somewhat, 50 c.c. of *warm* distilled water are run in through the condenser tube and the flask shaken gently until the glycerol triacetin is dissolved. (If necessary, the contents of the flask may be slightly heated, but not boiled, since acetin is volatile in steam.)

The solution is filtered into a wide-necked litre flask, allowed to cool completely and then carefully neutralized with 2 per cent. caustic soda solution, using phenolphthaleïn as indicator. During this operation the flask should be constantly shaken to avoid any local excess of free alkali. The neutral point is reached when the pale yellow colour of the solution just changes to reddish-yellow.

25 c.c. of 10 per cent. caustic soda solution are then added, the solution boiled for fifteen minutes and the excess of alkali titrated back with normal acid. Similarly, 25 c.c. of the caustic soda solution are boiled and titrated. The difference between the titrations corresponds to the amount of alkali consumed in the saponification of the triacetin produced; 3 molecules of sodium hydroxide correspond to 1 molecule of glycerin.

When glycerin is heated with acetic anhydride in presence of a dehydrating agent such as anhydrous sodium acetate, it is esterified quantitatively to triacetin (the glycerol ester of acetic acid), thus:



$$2C_3H_5(OH)_3 + 3\begin{matrix}CH_3CO\\CH_3CO\end{matrix}{>}O = 2C_3H_5(CH_3COO)_3 + 3H_2O.$$

The sodium acetate should be quite free from moisture. It is prepared by dehydrating the crystalline salt $CH_3COONa.3H_2O$. When this salt is heated it dissolves in its own water of crystallization, of which at first only 2 molecules are expelled. At this stage the monohydrate $CH_3COONa.H_2O$ solidifies, but on heating more strongly it melts and gradually loses the remaining water. The anhydrous acetate generally has a brown tinge, which, however, is of no consequence.

It is essential that the neutralization of the free acetic acid, formed from the excess of anhydride used, be done carefully, owing to the fact that triacetin is very readily saponified by free alkali. If the titration has been carried beyond the neutral point and the solution is distinctly pink, the test must be repeated, as the excess of alkali cannot be titrated back.

The saponification of triacetin by caustic alkali is expressed by the equation

$$C_3H_5(CH_3COO)_3 + 3NaOH = C_3H_5(OH)_3 + 3CH_3COONa.$$

In addition to glycerol, the organic impurities and ash are usually determined.

B.—Distilled Glycerin, Chemically Pure or Dynamite Glycerin.

1. Determination of Glycerol.—0·2 to 0·3 gr. of the concentrated glycerin, or a corresponding amount of dilute glycerin, is mixed in a litre flask with about 250 c.c. of water and made strongly alkaline by the addition of 10 grs. of solid caustic potash. Finely powdered potassium permanganate is then added to the cold solution, with constant shaking, until the colour changes from green to blue or nearly black. After allowing to stand for thirty minutes, the excess of permanganate is decomposed by adding hydrogen peroxide until the colour is completely discharged, with precipitation of manganese dioxide. The excess of hydrogen peroxide is removed by boiling for thirty minutes, after which the solution is cooled and diluted to the mark; 500 c.c. of this solution are passed through a *dry* filter, acidified with sulphuric acid, heated to 60° C. and titrated with decinormal permanganate.

Glycerol in strongly alkaline solution is oxidized by permanganate to oxalic acid, the reaction taking place quantitatively in the cold:

$$C_3H_5(OH)_3 + 3O_2 = (COOH)_2 + CO_2 + 3H_2O.$$

In this case 1 molecule of glycerol yields 1 molecule of oxalic acid; hence 1 c.c. of decinormal potassium permanganate corresponds to $4{\cdot}6 \times 0{\cdot}001 = 0{\cdot}0046$ gr. of glycerol.

Another method consists in oxidizing glycerol in sulphuric acid solution to carbon dioxide by treatment with permanganate or chromic acid, and either absorbing the gas in a soda-lime tube or titrating back the excess of oxidizing agent.

These oxidation methods give reliable results only with pure glycerol; crude glycerol contains impurities which likewise take part in the reaction.

In practice the percentage of glycerol in a sample of highly concentrated pure glycerin is generally estimated by determining the specific gravity. The acetin method may also be used. For samples of dilute (pure) glycerin the oxidation method is employed, since in this case the specific gravity cannot be determined with sufficient accuracy, and the acetin method would involve a preliminary concentration.

A reduction method for determining glycerol has been devised which, although somewhat complicated, gives accurate results. The sample is heated with concentrated hydriodic acid, by which the glycerol is reduced to isopropyl iodide—

$$CH_2OH.CHOH.CH_2OH + 5HI = CH_3.CHI.CH_3 + 3H_2O + 2I_2.$$

The iodine liberated in the reaction is then combined by the addition of phosphorus, and the isopropyl iodide distilled into an alcoholic solution of silver nitrate, when the iodine is precipitated as silver iodide, filtered off and weighed.

Glycerin intended for the manufacture of dynamite must be of superior quality. It should contain at least 98 per cent. of glycerol, and be quite free from lime, magnesia, alumina, chlorine, arsenic, organic colouring matter and acids. Not all glycerin, even of this concentration and purity, is suitable for nitration. Every commercial sample must be submitted to a special nitration test similar in all respects to the nitrating process employed on a large scale.

Glycerin is obtained as a by-product in the manufacture of fatty acids and soap. The glycerin waters, from the various saponification processes (p. 207), containing 12 to 15 per cent.

of glycerin, are purified by treatment with lime, sulphuric acid, barium hydroxide, or oxalic acid, and then concentrated to 80 to 90 per cent. by evaporation in vacuum-pans. The purification and concentration of the mother-liquors from the soap-making process, which contain only 5 to 8 per cent. of glycerin and about 10 per cent. of common salt, together with some free alkali and soap, is more difficult.

Crude glycerin is divided into various grades according to its origin. The best quality is *saponification glycerin,* which is obtained from the autoclave process; it contains only 0·3 to 0·5 per cent. of mineral matter and has a sweet taste. The product derived from the acid saponification process is known as *distillation glycerin;* it contains on an average 2 to 3·5 per cent. of mineral substances and has usually an unpleasant odour and a sharp, astringent taste. The most impure product is that extracted from the soap liquors, called *soap-lye glycerin,* which contains 10 per cent. of mineral matter, chiefly common salt, and generally possesses a disagreeable smell and taste.

The crude glycerin is purified by distillation or by filtration through animal charcoal. Chemically pure glycerin can only be obtained by the former process; the distillation is performed either in a vacuum apparatus or by means of superheated steam, with subsequent concentration.

Glycerin is used in pharmaceutical preparations, in the textile industry for " sizes," and for various other purposes. By far the greater portion, however, is employed in the manufacture of nitroglycerin and other explosives.

25. LUBRICANTS.

A.—Mineral Oils.

1. Determination of the Viscosity (Engler's Viscosimeter) —(*a*) *Calibration of the Apparatus with Water.*—The reservoir *A* (Fig. 34) is thoroughly cleansed with alcohol and ether. The outflow tube *a* is closed by means of the stopper *b* (consisting of a brass sphere attached to a rod), and the vessel *A* filled with distilled water up to the points of three pins, *c*, projecting from the walls. The apparatus should be

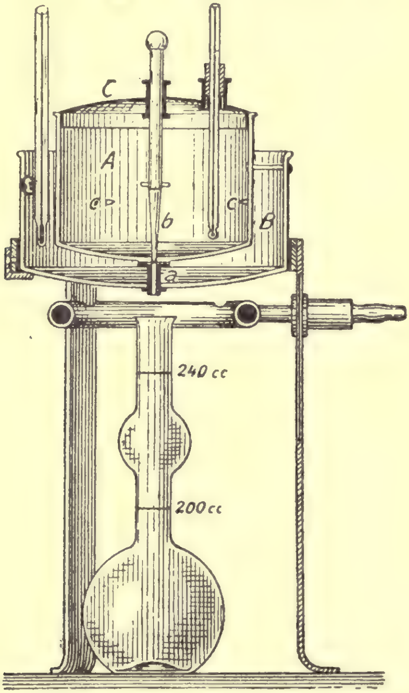


FIG. 34.

carefully levelled so that the water surface is just touched by all three pins. The annular space B is now filled to the top with water, the lid C set on, and the temperature of the apparatus adjusted to 20° C. When the temperature is uniform the stopper is raised (taking care to avoid shaking) and the time required for 200 c.c. of water to flow through the orifice ascertained by means of a stop-watch reading to one-fifth of a second. The experiment is repeated several times, and the readings should agree to within half a second. The average time of flow in a suitable apparatus is from fifty to fifty-two seconds.

(*b*) *Time of Flow of the Oil.*—The reservoir is dried with a small quantity of alcohol and ether, filled to the mark with oil and the time required for the oil to pass through the orifice determined as before. The sample of oil must not contain solid impurities and, if necessary, should be passed through a sieve of 0·3 sq. mm. mesh before use. Although the instrument is calibrated with water at one temperature only—viz., 20° C.—the viscosity of the oil should be determined at various temperatures. Oils which are not exposed to high temperatures when in use, such as spindle and machine oils, are examined at 20° C. and 50° C., and sometimes at intermediate temperatures. Steam-cylinder oils are tested at 50° C. and 100° C. For experiments above 100° C. the outer bath B is filled with a suitable liquid and heated to the required temperature by means of a ring burner attached to the apparatus. The bulk of the oil under examination is poured into the inner cylinder, and after this has reached the required temperature a further small portion is added to bring it up to the mark. In the case of highly viscous oils, a less volume (100 or 50 c.c.) can be used.

The ratio of the time of flow of an oil at a given temperature to that of water at 20° C. expresses the number of "Engler degrees."

Example: Water at 20° C. passed through the orifice in 51 seconds; an equal volume of oil at 40° C. required 337 seconds. The viscosity of the oil at 40° C. is $\frac{337}{51} = 6{\cdot}61°$ Engler.

The pale spindle oils used for lubricating spinning and other fine machinery have the lowest viscosities—viz., 5° to 10° Engler. Light machine oils, dynamo and motor oils should range from 13° to 25°, heavy machine oils 25° to 45° Engler. Oils of the highest viscosity (from 50° to 60° Engler at 50° C.) are required for steam-cylinder lubrication.

2. Determination of the Flash-Point and the Ignition-Point.—The *flash-point* of an oil is the temperature at which vapour is produced in sufficient quantity to explode with air when brought in contact with a flame. The lowest temperature at which the oil will continue to burn after the flame has been applied to its surface for a few seconds is called the *ignition-point.*

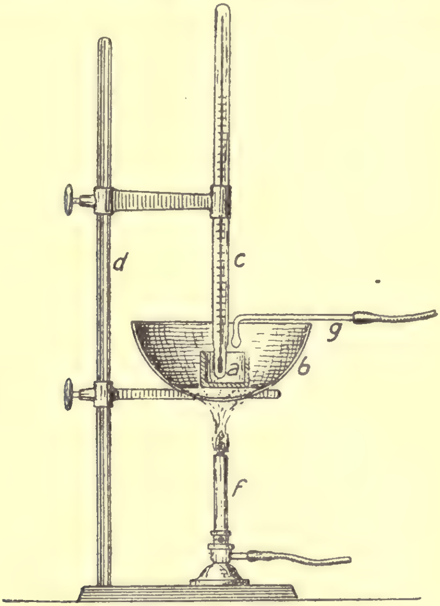


Fig. 35.

These determinations are made by one of the following methods, according to the nature of the material under examination:

(*a*) *Light Machine Oils.*—A porcelain crucible *a* (Fig. 35), 4 cm. in diameter and 4 cm. deep, rests upon a layer of about 1·5 cm. of sand at the bottom of a half-spherical iron dish of some 18 cm. diameter. It is filled to about 1 cm. below the rim with the oil under investigation. The bulb of the thermometer *c* must be completely immersed in the oil. The oil is heated rapidly to the neighbourhood of the flash-point and then more carefully at the rate of 2° to 5° C. per minute. From time to time an *inverted* flame about 10 mm. long is passed slowly over the crucible at a distance of 3 or 4 mm. above the surface of the oil. The flame should remain over the crucible for about four seconds without coming into contact with the oil or the sides of the vessel. Up to 145° C. the test is made at intervals of 5° C.; above this temperature at every degree. The flash-point is reached when a " flash " or slight explosion is observed.

The heating is then continued, the jet being held *horizontally* and passed across the crucible immediately above the rim, taking one to two seconds in transit. When the oil ignites and continues to burn after the removal of the flame, the ignition-point has been reached.

(*b*) *Heavy Machine Oils and Cylinder Oils.*—The crucible is embedded in a sand-bath to the level of the oil within. The lighting jet, 10 mm. in length, is held horizontally and passed across the crucible just above the rim once in each direction.

Machine oils are filled to 1 cm., cylinder oils to 1·5 cm., below the rim of the crucible. In other respects the procedure is the same as in (*a*).

The flash-points and ignition-point of oils are not physical constants. The values obtained are largely influenced by the form of apparatus employed and the manner in which the experiment is performed, but they furnish a useful means of comparison when the tests are carried out under identical conditions. In practice the determination is generally made in a closed apparatus, the Pensky-Martens apparatus being most frequently employed (*vide* Boverton Redwood, "Treatise on Petroleum," 3rd ed., 1913, vol. ii., p. 267). As a rule the flash-points obtained in a closed vessel are considerably lower than those found by means of the crude apparatus described above.

The flash-point gives an indication of the volatility of the oil; the less readily an oil vaporizes, the more suitable is it for lubricating purposes. Oils containing volatile matter undergo change of composition when in use and the vapours evolved are liable to take fire.

The flash-point of the lighter machine oils should not be below 145° C., that of steam-cylinder oils not below 220° C.

3. Determination of Free Acids—(*a*) *Light-Coloured Oils.*—10 c.c. of the oil are pipetted into an Erlenmeyer flask and mixed with 100 c.c. of a mixture of ether and alcohol (4 : 1) which has been previously used to wash out the pipette. The solution is titrated with decinormal alcoholic caustic potash solution until a faint red coloration is obtained with phenolphthaleïn.

(*b*) *Dark Oils.*—If the oils are so dark that the colour change with phenolphthaleïn cannot be properly observed, the dye Alkali blue 6B or other suitable dye may be used. If a sufficiently sharp indication be not given by these dyes, proceed as in (*c*).

(*c*) *Artificially Coloured Oils.*—10 c.c. of the oil are dissolved in petroleum ether and well shaken with a decinormal alcoholic solution of caustic potash (50 per cent. aqueous alcohol). Phenolphthaleïn is then added, and the solution titrated until the colour of the alkaline layer is discharged.

If the oil contains only a very small amount of free acid, 50 or 100 c.c. should be taken for the analysis.

The result of the titration is expressed as the *acid value* of the oil, which, as in other cases, represents the number of milligrams of potassium hydroxide required to neutralize the acid in 1 gr. of the oil.

It is sufficient for ordinary purposes to measure the volume of the sample instead of weighing. The average specific gravity of mineral oils may be taken as 0·915. If 10 c.c. of oil be taken for the analysis, 1 c.c. of decinormal potash corresponds to an acid value of $\frac{5 \cdot 6}{9 \cdot 15} = 0 \cdot 61$.

The natural mineral oils contain, in addition to naphthenic acids, resinous substances which give an acid reaction. These are almost completely removed by refining. The acid value of pale refined oils is often zero and should not exceed 0·4, while the acidity of darker oils may be as high as 4·0. Oils adulterated with substances possessing higher acid values, such as fatty oils and more especially the resinic acids, exhibit abnormal acidity. Mineral oils occasionally contain free mineral acid or free alkali, as the result of faulty refining. In testing for free mineral acid (which can only be sulphuric acid used in refining the crude oil), 100 c.c. of the sample are shaken in a tap funnel with 200 c.c. of hot water and allowed to stand until the separation into two layers is complete. On adding methyl orange to the aqueous extract, a red coloration is produced in presence of sulphuric acid. The amount of acid may also be determined quantitatively. A good lubricating oil should not contain the slightest trace of free mineral acid. [To prevent confusion, it should be observed that the practice of expressing the acidity of a lubricating oil in terms of SO_3, instead of in the form of an acid value, is still common. In this case it is obvious that the actual presence of sulphuric acid is not to be inferred.] Similarly, the free alkali can be detected by adding phenolphthaleïn to the aqueous extract of the oil. In this connection it should be borne in mind that if the oil is adulterated with soap, the latter undergoes hydrolysis, producing a red coloration with phenolphthaleïn. For the detection of soap in lubricating oil, see p. 219.

4. Determination of Saponifiable Adulterants—(*a*) *Resin.*—Of the resins, only colophony need be considered, and this has a very high acid value. If the acid value of the oil is below 0·3 for a light-coloured oil, or below 4·0 for a dark oil, resin is probably absent.

Qualitative Test.—A few c.c. of the oil are warmed and shaken with an equal volume of 70 per cent. alcohol. After cooling, the alcoholic layer is separated into a porcelain dish and evaporated on the water-bath. The presence of resin is indicated by a viscid resinous deposit, which is further tested by the Liebermann-Storch reaction (p. 201).

The resinous substances which occur naturally in unadulterated mineral oils do not give this reaction. Good lubricating oil should be free from colophony and in most cases a qualitative examination is sufficient. For the quantitative determination of resin, the oil is extracted with caustic soda solution, the resin soap decomposed with hydrochloric acid and the separated resin acids weighed. When soaps, fats and resins are all present in the sample, the oil is first saponified with alcoholic potash and the soaps, after expelling the alcohol, separated from the unsaponifiable mineral oils by treating with petroleum ether. The soaps are then dissolved in water, acidified with hydrochloric acid, extracted with ether and the mixture of fatty acids and resin separated by Twitchell's method (p. 208) by esterifying the fatty acids with alcoholic hydrochloric acid.

(*b*) *Soap—Qualitative Test.*—When an oil containing soap is shaken with water, a thick white emulsion is formed which, owing to hydrolysis, produces a red coloration with phenolphthaleïn. This emulsion differs from that produced by a viscous oil, inasmuch as the former disappears on the addition of a mineral acid. The presence of sodium and potassium in the acid solutions can also be detected. Lime soaps or aluminium soaps are similarly detected.

Quantitative Examination.—10 c.c. of the oil are washed into a separating funnel with 40 to 60 c.c. of petroleum ether and well shaken with dilute hydrochloric acid, which is added in small portions until the aqueous layer is distinctly acid. The acid layer is then run off and the petroleum-ether layer washed repeatedly with water until the washings no longer show an acidic reaction. The acid value of the petroleum-ether solution is then determined as described in (3). (Light-coloured oils require the addition of a small quantity of alcohol.) The difference between the value thus obtained and the original acid value gives the amount of fatty acid in the soap contained in the oil. In general, a sufficiently accurate result is obtained by taking the mean molecular weight of these fatty acids as 275. In order to calculate the amount of soap from the free acids, it is necessary to ascertain the nature of the soap base; this is done by submitting the hydrochloric acid extract of the lubricating oil to a qualitative test.

Calculation of Results.—Suppose that for every 10 c.c. of oil, 2·5 c.c. of decinormal KOH are required in the direct determination of the acid value and 17·8 c.c. after treatment with hydrochloric acid. The base extracted with hydrochloric acid is found to be sodium. The molecular weight of the sodium soap is then (fatty acid $-$ H $+$ Na) $275-1+23=297$. Hence 1 c.c. of decinormal alkali corresponds to 0·0297 gr. of soap, and 10 c.c. of the oil ($=$9·15 grs.)

contain $(17 \cdot 8 - 2 \cdot 5) \times 0 \cdot 0297 = 0 \cdot 454$ gr., or 4·97 per cent. by weight of soap.

When a mineral oil adulterated with soap is shaken with dilute mineral acid, the latter combines with the soap base and the liberated fatty acids dissolve in the oil; hence, after removing the excess of mineral acid by washing, the original acidity of the oil is increased by an amount corresponding to the fatty acids from the soap.

Lubricating oils are thickened by the addition of a small quantity of soap. Read also the notes on Solid Lubricants (pp. 222, 224).

(*c*) *Fats, Oils and Waxes—Qualitative Test.*—3 to 4 c.c. of the lubricating oil are heated with a fragment of sodium hydroxide about the size of a pea in a test-tube immersed in an oil-bath at 230° to 240° C. for fifteen minutes. The test-tube is then removed and allowed to cool. If a fat or wax be present, a froth of soap is formed on the surface during the heating, or the oil gelatinizes on cooling. This test is very sensitive; according to Holde, as little as 0·5 per cent. of fat or wax may be detected in a light-coloured, mobile mineral oil, about 2 per cent. in a dark lubricating oil, and about 1 per cent. in a cylinder oil. If it be necessary to test for still smaller amounts, the following quantitative determination should be made:

Quantitative Determination of Fat and Wax.—(i.) If wax or *small quantities* of fat are present, the saponification value of the lubricating oil is determined; 5 to 10 grs. of the oil are mixed with 25 c.c. of seminormal alcoholic potash solution and 25 c.c. of benzene in a flask provided with a reflux condenser, and boiled on the water-bath for thirty minutes. After cooling, the excess of alkali is titrated back with seminormal hydrochloric acid, using phenolphthaleïn as indicator. In calculating the result, the amount of alkali used to neutralize the free acid, as found in (3), must be deducted. The average saponification value of the fats in question may be taken as 185. Of the waxes, only wool wax is likely to be present and this is easily recognized by its peculiar odour. The saponification value (p. 180) of wool wax is 102. If the saponification value found by the above titration is 15·3, this will correspond to $\frac{15{\cdot}3 \times 100}{185} = 8{\cdot}3$ per cent. of fat, or $\frac{15{\cdot}3 \times 100}{102} = 15{\cdot}0$ per cent. of wool wax.

(ii.) If a comparatively large amount of fat be present, 7 to 10 grs. of the oil are saponified with 50 c.c. of seminormal caustic potash and extracted by shaking with petroleum ether. The extract is evaporated and the residue weighed. The difference in weight of the oil taken for analysis and the residual unsaponifiable matter obtained gives the amount of saponifiable fat.

The latter method cannot be used if wool wax be present, since this wax itself contains a large amount of unsaponifiable matter (see p. 196). The wax alcohols can be separated by esterification with acetic anhydride, but this separation is tedious and incomplete.

5. Determination of Unsaponifiable Added Oils (Resin Oils, etc.)—(*a*) *Resin Oils.*—Resin oils, which in general exhibit the same reactions as resin (resin acids), differ from the latter in that they are unsaponifiable. If the Liebermann-Storch reaction (p. 201) gives a positive result, the oils are tested further in a polarimeter (dark oils are first clarified by treatment with animal charcoal). Resin oils, like resin, are strongly *dextrorotatory*, while mineral oils are as a rule optically inactive.

When colophony (p. 201) is submitted to dry distillation, it decomposes with the formation of volatile resin alcohols and heavy resin oils consisting of hydrocarbons of high boiling-point (upwards of 300° C.), while coke remains in the retort. The crude resin oil is always contaminated with resin acids carried over during the distillation; hence mineral oils adulterated with unrefined resin oils possess high acid values. The resin oils are used chiefly in the preparation of solid lubricants (*q.v.*).

(*b*) *Coal-Tar Oils.*—These oils are distinguished by the characteristic smell of creosote. They differ from mineral oils in that they are completely soluble in cold alcohol and also in concentrated sulphuric acid when heated gently on the water-bath.

B.—Solid Lubricants.

Determination of the Dropping-Point (Ubbelohde's Method).—By the "dropping-point" of a solid lubricant is meant the temperature at which a drop of the melted substance falls from a uniformly heated test portion under suitable conditions. The apparatus (Fig. 36) used in this determination consists of a small open cup, *e*, with a hole 3 mm. in diameter at the bottom, attached to the bulb of a thermometer by means of a cylindrical brass casing, *b*. The casing has a small perforation at *c*. The experiment is performed in the following way: The cup is removed and filled with the substance to be tested, which is levelled above and below. It is then inserted in the metal cylinder up to the three projecting pins, *d*. Solid substances which might injure the thermometer when it is pressed into the container should first be softened by warming in the cup placed upon a sheet of glass. The thermometer is then supported by a cork in a wide test-tube (4 cm. diameter) which is immersed in a large beaker filled with water. The water is heated at the uniform rate of about 1° C. per minute; the temperature at which the substance begins to pass through the hole in the cup indicates the *softening-point*, that at which the first drop falls the *dropping-point*.

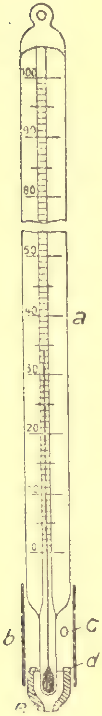


FIG. 36.

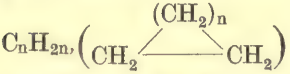
Those solid lubricants which consist of a mixture of fats, or of fats with soap or other substances (*vide infra*), do not exhibit a sharp melting-point. They gradually soften until finally a drop is formed. The dropping-point determination is the only means of testing the mechanical action of solid lubricants, and is therefore of prime importance in the valuation of lubricating greases. The chemical examination must be adapted to suit particular cases, since the composition of solid lubricants differs greatly. As a rule the quantitative test used for mineral oils is applied, preceded by a qualitative examination.

The most important of the raw materials used in the manufacture of lubricants is the residue obtained from the distillation of petroleum after the removal of benzine and illuminating oils. The richest oil wells are found in North America and Russia (Baku). Considerable supplies are also obtained in Galicia and Rumania, the Dutch East Indies (Sumatra, Java), British East Africa and Japan.

In the winning of petroleum, bore-holes are sunk into the oil-bearing strata, from which the oil gushes under pressure or is pumped up.

Formerly petroleum was supposed to be of inorganic origin, formed by the interaction of water under high pressure with carbides, but the view now most generally accepted attributes its formation to the decomposition of vegetable, and possibly in certain cases animal, residues, since natural petroleum is frequently found in association with these substances, and sometimes contains a small amount of nitrogen.

Natural petroleum oils consist chiefly of hydrocarbons, which are present to the extent of 70 to 90 per cent., but the composition of crude oils obtained from different sources is by no means uniform. In the American and Galician petroleums the paraffins C_nH_{2n+2} predominate, while the Russian oils contain principally naphthenes — *i.e.*, ring compounds of the formula $C_nH_{2n}, \left(\overset{(CH_2)_n}{CH_2 \quad CH_2}\right)$ and, in addition, a not inconsiderable quantity of the isomeric olefines and other unsaturated hydrocarbons.



In addition to hydrocarbons, all crude oils contain varying amounts of naphtho-acids, fatty acids, phenols, nitrogen and sulphur compounds.

The crude oil is first distilled. Impure benzine passes over up to 150° C. and illuminating oil (kerosene) between 150° C. and 300° C. The fraction boiling above 300° C. (amounting to only 10 to 20 per cent. in American oils, but 55 to 70 per cent. in Russian, and as much as 70 to 90 per cent. in Galician oils) is unsuitable for lighting, and is utilized as a fuel (Masut), or worked up as a lubricant. In the latter case the residues are refined by distillation *in vacuo*, or in a current of superheated steam, since distillation under atmospheric pressure is accompanied by a partial decomposition and a diminution of the viscosity. After the distillation a heavy dark resin remains. The oils now have a pale colour; they are submitted to further purification by chemical treatment, first with concentrated sulphuric acid, by which a part of the impurities are converted into sulphonic acids soluble in water, while others are oxidized or resinified and the unsaturated hydrocarbons are dissolved. This is followed by a second treatment with caustic soda, which removes the free organic acids as petroleum soaps and also removes any remaining traces of sulphuric or sulphurous acid. Finally the oils are washed with water. The oils refined in this way are used as spindle oils, machine oils and cylinder oils, according to their viscosity.

For the lubrication of axle-bearings—*e.g.*, on railway carriages—the undistilled dark-coloured oils purified only by the acid and caustic soda treatment are mostly employed. This treatment is sufficient when the oil contains only a small amount of paraffin wax, as in the case of Russian oils. Oil residues containing much paraffin, such as are obtained from American and East Indian petroleums, deposit this substance in the solid condition on cooling. These are submitted to a preliminary artificial cooling to freeze out the paraffin wax.

Mineral oils are superior to fatty oils in that they do not become rancid. On account of their comparative cheapness they have to a large extent displaced the fatty oils, which a few decades ago were practically the only substances employed as lubricants.

The principal fats and oils at present used for lubricating purposes are the cheap rape oil (colza oil), mustard oil, castor oil and olive oil—the last two especially on Italian ships—tallow, used for greasing the stuffing-boxes of steam cylinders, wool fat and train oils (fish oils). Carefully refined neat's-foot oil and bone oils, which do not readily become rancid, are used for oiling watches and scientific instruments.

The viscosity of fatty oils varies within much narrower limits than is the case with mineral oils. At 20° C. rape, olive and bone oils have a viscosity of 11° to 15° Engler, the semi-drying oils 9·3° to 10·4° E. and drying oils 6·8° to 8·3° E. Castor oil alone possesses an abnormally high viscosity—viz., 139° to 140° E. On the other hand, the flash-points of the fatty oils are usually much higher than those of the mineral oils, so that the former are specially suitable, and are often preferred, for the lubrication of hot running machine parts, such as the high-pressure cylinders of locomotives and marine engines.

Mixtures of mineral and fatty oils are also employed as lubricants. In these mixtures "blown oils"—*i.e.*, artificially thickened fatty oils—are used to increase the viscosity, since castor oil, which, on account of its very high viscosity, might appear to be suitable for this purpose, does not mix with mineral oils. The artificial thickening is accomplished by exposing semi-drying oils such as rape oil or cotton-seed oil, at a temperature of 70° to 100° C., to a current of air or oxygen, whereby the density of the oil is increased by partial oxidation. Since oils treated in this way bear a certain resemblance to castor oil, but are miscible with mineral oils, they are sometimes called "soluble castor oil." The *solid lubricants* are composed chiefly of admixtures of the soaps of the alkali metals, calcium, aluminium and zinc, with fats, fatty oils, mineral oils, resin oils, or coal-tar oils. A little water is usually added with the soap. Solid lubricants also frequently contain loading substances, such as powdered soapstone (steatite) and graphite; the inferior qualities also contain free lime, finely ground barytes and other adulterants.

APPENDIX

ATOMIC WEIGHTS.

O = 16·000.

Aluminium	Al	27·1	Lithium	Li	6·94
Antimony	Sb	120·2	Magnesium	Mg	24·32
Arsenic	As	74·96	Manganese	Mn	54·93
Barium	Ba	137·37	Mercury	Hg	200·0
Bismuth	Bi	208·0	Molybdenum	Mo	96·0
Boron	B	11·0	Nickel	Ni	58·68
Bromine	Br	79·92	Nitrogen	N	14·01
Cadmium	Cd	112·40	Oxygen	O	16·00
Calcium	Ca	40·09	Phosphorus	P	31·04
Carbon	C	12·00	Platinum	Pt	195·2
Chlorine	Cl	35·46	Potassium	K	39·10
Chromium	Cr	52·00	Silicon	Si	28·3
Cobalt	Co	58·97	Silver	Ag	107·88
Copper	Cu	63·57	Sodium	Na	23·00
Fluorine	F	19·0	Strontium	Sr	87·63
Gold	Au	197·2	Sulphur	S	32·06
Hydrogen	H	1·008	Tin	Sn	118·7
Iodine	I	126·92	Titanium	Ti	48·1
Iron	Fe	55·84	Tungsten	Wo	184·0
Lead	Pb	207·20	Zinc	Zn	65·37

WATER OF CRYSTALLIZATION OF SOME FREQUENTLY USED SALTS.

$BaCl_2$.2 aq.
$Ba(OH)_2$.8 aq.
$FeSO_4$.7 aq.
$(NH_4)_2SO_4.FeSO_4$.6 aq.
$(NH_4)_2SO_4.Fe_2(SO_4)_3$.24 aq.
(Iron ammonium alum.)
$K_4Fe(CN)_6$.3 aq.
$K_2SO_4.Al_2(SO_4)_3$.24 aq.
$MgCl_2$.6 aq.
$NH_4Cl. MgCl_2$.6 aq.
$MgSO_4$.7 aq.
$MnSO_4$.7 aq.
NH_4NaHPO_4.4 aq. (Microcosmic salt).
Na_2CO_3.10 aq.
Na_2HPO_4.12 aq.
Na_2S. 9 aq.
$Na_2S_2O_3$.5 aq.
Na_2SO_4.10 aq.
$SnCl_2$.2 aq.
$ZnSO_4$.7 aq.

SPECIFIC GRAVITY TABLES.

1. Acids.

Hydrochloric Acid (Lunge and Marchlewski).

Sp. Gr. *at* $\frac{15^\circ}{4^\circ}$	% HCl	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% HCl	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% HCl	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% HCl
1·000	0·16	1·060	12·19	1·120	23·82	1·165	32·49
1·005	1·15	1·065	13·19	1·125	24·78	1·170	33·46
1·010	2·14	1·070	14·17	1·130	25·75	1·171	33·65
1·015	3·12	1·075	15·16	1·135	26·70	1·175	34·42
1·020	4·13	1·080	16·15	1·140	27·66	1·180	35·39
1·025	5·15	1·085	17·13	1·1425	28·14	1·185	36·31
1·030	6·15	1·090	18·11	1·145	28·61	1·190	37·23
1·035	7·15	1·095	19·06	1·150	29·57	1·195	38·16
1·040	8·16	1·100	20·01	1·152	29·95	1·200	39·11
1·045	9·16	1·105	20·97	1·155	30·55		
1·050	10·17	1·110	21·92	1·160	31·52		
1·055	11·18	1·115	22·86	1·163	32·10		

Perchloric Acid (van Emster).

Sp. Gr. *at* $\frac{15^\circ}{4^\circ}$	% $HClO_4$	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% $HClO_4$	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% $HClO_4$	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% $HClO_4$
1·020	3·6	1·200	29·3	1·380	47·5	1·560	61·5
1·040	6·9	1·220	31·6	1·400	49·2	1·580	63·0
1·060	10·1	1·240	33·9	1·420	50·9	1·600	64·5
1·080	13·1	1·260	36·0	1·440	52·5	1·620	66·0
1·100	16·0	1·280	38·1	1·460	54·1	1·640	67·5
1·120	18·9	1·300	40·1	1·480	55·6	1·660	69·0
1·140	21·6	1·320	42·0	1·500	57·1	1·675	70·2
1·160	24·3	1·340	43·9	1·520	58·5		
1·180	26·8	1·360	45·7	1·540	60·0		

Nitric Acid (Lunge and Rey).

Sp. Gr. *at* $\frac{15^\circ}{4^\circ}$	% HNO_3	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% HNO_3	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% HNO_3	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% HNO_3
1·000	0·10	1·025	4·60	1·050	8·99	1·075	13·15
1·005	1·00	1·030	5·50	1·055	9·84	1·080	13·95
1·010	1·90	1·035	6·38	1·060	10·68	1·085	14·74
1·015	2·80	1·040	7·26	1·065	11·51	1·090	15·53
1·020	3·70	1·045	8·13	1·070	12·33	1·095	16·32

Nitric Acid (Lunge and Rey)—Continued.

Sp. Gr. *at* $\frac{15^\circ}{4^\circ}$	% HNO_3	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% HNO_3	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% HNO_3	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% HNO_3
1·100	17·11	1·230	36·78	1·355	56·66	1·480	86·05
1·105	17·89	1·235	37·53	1·360	57·57	1·485	87·70
1·110	18·67	1·240	38·29	1·365	58·48	1·490	89·60
1·115	19·45	1·245	39·05	1·370	59·39	1·495	91·60
1·120	20·23	1·250	39·82	1·375	60·30	1·500	94·09
1·125	21·00	1·255	40·58	1·380	61·27	1·501	94·60
1·130	21·77	1·260	41·34	1·3833	61·92	1·502	95·08
1·135	22·54	1·265	42·10	1·385	62·24	1·503	95·55
1·140	23·31	1·270	42·87	1·390	63·23	1·504	96·00
1·145	24·08	1·275	43·64	1·395	64·25	1·505	96·39
1·150	24·84	1·280	44·41	1·400	65·30	1·506	96·76
1·155	25·60	1·285	45·18	1·405	66·40	1·507	97·13
1·160	26·36	1·290	45·95	1·410	67·50	1·508	97·50
1·165	27·12	1·295	46·72	1·415	68·63	1·509	97·84
1·170	27·88	1·300	47·49	1·420	69·80	1·510	98·10
1·175	28·63	1·305	48·26	1·425	70·98	1·511	98·32
1·180	29·38	1·310	49·07	1·430	72·17	1·512	98·53
1·185	30·13	1·315	49·89	1·435	73·39	1·513	98·73
1·190	30·88	1·320	50·71	1·440	74·68	1·514	98·90
1·195	31·62	1·325	51·53	1·445	75·98	1·515	99·07
1·200	32·36	1·330	52·37	1·450	77·28	1·516	99·21
1·205	33·09	1·3325	52·80	1·455	78·60	1·517	99·34
1·210	33·82	1·335	53·22	1·460	79·98	1·518	99·46
1·215	34·55	1·340	54·07	1·465	81·42	1·519	99·57
1·220	35·28	1·345	54·93	1·470	82·90	1·520	99·67
1·225	36·03	1·350	55·79	1·475	84·45		

Sulphuric Acid (Lunge and Isler).

Sp. Gr. *at* $\frac{15^\circ}{4^\circ}$	% H_2SO_4	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% H_2SO_4	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% H_2SO_4	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% H_2SO_4
1·000	0·09	1·045	6·67	1·090	12·99	1·135	18·96
1·005	0·83	1·050	7·37	1·095	13·67	1·140	19·61
1·010	1·57	1·055	8·07	1·100	14·35	1·145	20·26
1·015	2·30	1·060	8·77	1·105	15·03	1·150	20·91
1·020	3·03	1·065	9·47	1·110	15·71	1·155	21·55
1·025	3·76	1·070	10·19	1·115	16·36	1·160	22·19
1·030	4·49	1·075	10·90	1·120	17·01	1·165	22·83
1·035	5·23	1·080	11·60	1·125	17·66	1·170	23·47
1·040	5·96	1·085	12·30	1·130	18·31	1·175	24·12

Sulphuric Acid (Lunge and Isler)—Continued.

Sp. Gr. *at* $\frac{15^\circ}{4^\circ}$	% H_2SO_4	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% H_2SO_4	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% H_2SO_4	*Sp. Gr.* *at* $\frac{15^\circ}{4^\circ}$	% H_2SO_4
1·180	24·76	1·380	48·00	1·580	66·71	1·780	84·50
1·185	25·40	1·385	48·53	1·585	67·13	1·785	85·10
1·190	26·04	1·390	49·06	1·590	67·59	1·790	85·70
1·195	26·68	1·395	49·59	1·595	68·05	1·795	86·30
1·200	27·32	1·400	50·11	1·600	68·51	1·800	86·90
1·205	27·95	1·405	50·63	1·605	68·97	1·805	87·60
1·210	28·58	1·410	51·15	1·610	69·43	1·810	88·30
1·215	29·21	1·415	51·66	1·615	69·89	1·815	89·05
1·220	29·84	1·420	52·15	1·620	70·32	1·820	90·05
1·225	30·48	1·425	52·63	1·625	70·74	1·821	90·20
1·230	31·11	1·430	53·11	1·630	71·16	1·822	90·40
1·235	31·70	1·435	53·59	1·635	71·57	1·823	90·60
1·240	32·28	1·440	54·07	1·640	71·99	1·824	90·80
1·245	32·86	1·445	54·55	1·645	72·40	1·825	91·00
1·250	33·43	1·450	55·03	1·650	72·82	1·826	91·25
1·255	34·00	1·455	55·50	1·655	73·23	1·827	91·50
1·260	34·57	1·460	55·97	1·660	73·64	1·828	91·70
1·265	35·14	1·465	56·43	1·665	74·07	1·829	91·90
1·270	35·71	1·470	56·90	1·670	74·51	1·830	92·10
1·275	36·29	1·475	57·37	1·675	74·97	1·831	92·30
1·280	36·87	1·480	57·83	1·680	75·42	1·832	92·52
1·285	37·45	1·485	58·28	1·685	75·86	1·833	92·75
1·290	38·03	1·490	58·74	1·690	76·30	1·834	93·05
1·295	38·61	1·495	59·22	1·695	76·73	1·835	93·43
1·300	39·19	1·500	59·70	1·700	77·17	1·836	93·80
1·305	39·77	1·505	60·18	1·705	77·60	1·837	94·20
1·310	40·35	1·510	60·65	1·710	78·04	1·838	94·60
1·315	40·93	1·515	61·12	1·715	78·48	1·839	95·00
1·320	41·50	1·520	61·59	1·720	78·92	1·840	95·60
1·325	42·08	1·525	62·06	1·725	79·36	1·8405	95·95
1·330	42·66	1·530	62·53	1·730	79·80	1·8410	97·00
1·335	43·20	1·535	63·00	1·735	80·24	1·8415	97·70
1·340	43·74	1·540	63·43	1·740	80·68	1·8410	98·20
1·345	44·28	1·545	63·85	1·745	81·12	1·8405	98·70
1·350	44·82	1·550	64·26	1·750	81·56	1·8400	99·20
1·355	45·35	1·555	64·67	1·755	82·00	1·8395	99·45
1·360	45·88	1·560	65·08	1·760	82·44	1·8390	99·70
1·365	46·41	1·565	65·49	1·765	82·88	1·8385	99·95
1·370	46·94	1·570	65·90	1·770	83·32		
1·375	47·47	1·575	66·30	1·775	83·90		

Acetic Acid (*Oudemans*).

Sp. Gr. *at* $\frac{15^\circ}{15^\circ}$	%	*Sp. Gr.* *at* $\frac{15^\circ}{15^\circ}$	%	*Sp. Gr.* *at* $\frac{15^\circ}{15^\circ}$	%	*Sp. Gr.* *at* $\frac{15^\circ}{15^\circ}$	%
0·9992	0	1·0363	26	1·0631	52	1·0748	78
1·0007	1	1·0375	27	1·0638	53	1·0748	79
1·0022	2	1·0388	28	1·0646	54	1·0748	80
1·0037	3	1·0400	29	1·0653	55	1·0747	81
1·0052	4	1·0412	30	1·0660	56	1·0746	82
1·0067	5	1·0424	31	1·0666	57	1·0744	83
1·0083	6	1·0436	32	1·0673	58	1·0742	84
1·0098	7	1·0447	33	1·0679	59	1·0739	85
1·0113	8	1·0459	34	1·0685	60	1·0736	86
1·0127	9	1·0470	35	1·0691	61	1·0731	87
1·0142	10	1·0481	36	1·0697	62	1·0726	88
1·0157	11	1·0492	37	1·0702	63	1·0720	89
1·0171	12	1·0502	38	1·0707	64	1·0713	90
1·0185	13	1·0513	39	1·0712	65	1·0705	91
1·0200	14	1·0523	40	1·0717	66	1·0696	92
1·0214	15	1·0533	41	1·0721	67	1·0686	93
1·0228	16	1·0543	42	1·0725	68	1·0674	94
1·0242	17	1·0552	43	1·0729	69	1·0660	95
1·0256	18	1·0562	44	1·0733	70	1·0644	96
1·0270	19	1·0571	45	1·0737	71	1·0625	97
1·0284	20	1·0580	46	1·0740	72	1·0604	98
1·0298	21	1·0589	47	1·0742	73	1·0580	99
1·0311	22	1·0598	48	1·0744	74	1·0553	100
1·0324	23	1·0607	49	1·0746	75		
1·0337	24	1·0615	50	1·0747	76		
1·0350	25	1·0623	51	1·0748	77		

2. Alkalis.

Ammonium Hydroxide (*Lunge and Wiernik*).

Sp. Gr. *at* $\frac{15^\circ}{15^\circ}$	% NH_3	*Sp. Gr.* *at* $\frac{15^\circ}{15^\circ}$	% NH_3	*Sp. Gr.* *at* $\frac{15^\circ}{15^\circ}$	% NH_3	*Sp. Gr.* *at* $\frac{15^\circ}{15^\circ}$	% NH_3
1·000	0·00	0·986	3·30	0·972	6·80	0·958	10·47
0·998	0·45	0·984	3·80	0·970	7·31	0·956	11·03
0·996	0·91	0·982	4·30	0·968	7·82	0·954	11·60
0·994	1·37	0·980	4·80	0·966	8·33	0·952	12·17
0·992	1·84	0·978	5·30	0·964	8·84	0·950	12·74
0·990	2·31	0·976	5·80	0·962	9·35	0·948	13·31
0·988	2·80	0·974	6·30	0·960	9·91	0·946	13·88

Ammonium Hydroxide (Lunge and Wiernik)—Continued.

Sp. Gr. *at* $\frac{15^\circ}{15^\circ}$	% NH_3	*Sp. Gr.* *at* $\frac{15^\circ}{15^\circ}$	% NH_3	*Sp. Gr.* *at* $\frac{15^\circ}{15^\circ}$	% NH_3	*Sp. Gr.* *at* $\frac{15^\circ}{15^\circ}$	% NH_3
0·944	14·46	0·928	19·25	0·912	24·33	0·896	29·69
0·942	15·04	0·926	19·87	0·910	24·99	0·894	30·37
0·940	15·63	0·924	20·49	0·908	25·65	0·892	31·05
0·938	16·22	0·922	21·12	0·906	26·31	0·890	31·75
0·936	16·82	0·920	21·75	0·904	26·98	0·888	32·50
0·934	17·42	0·918	23·39	0·902	27·65	0·886	33·25
0·932	18·03	0·916	23·03	0·900	28·33	0·884	34·10
0·930	18·64	0·914	23·68	0·898	29·01	0·882	34·95

Caustic Potash (Lunge).

Sp. Gr. *at* 15°	% KOH	*Sp. Gr.* *at* 15°	% KOH	*Sp. Gr.* *at* 15°	% KOH	*Sp. Gr.* *at* 15°	% KOH
1·007	0·9	1·116	13·8	1·252	27·0	1·424	40·9
1·014	1·7	1·125	14·8	1·263	28·0	1·438	42·1
1·022	2·6	1·134	15·7	1·274	28·9	1·453	43·4
1·029	3·5	1·142	16·5	1·285	29·8	1·468	44·6
1·037	4·5	1·152	17·6	1·297	30·7	1·483	45·8
1·045	5·6	1·162	18·6	1·308	31·8	1·498	47·1
1·052	6·4	1·171	19·5	1·320	32·7	1·514	48·3
1·060	7·4	1·180	20·5	1·332	33·7	1·530	49·4
1·067	8·2	1·190	21·4	1·345	34·9	1·540	50·6
1·075	9·2	1·200	22·4	1·357	35·9	1·563	51·9
1·083	10·1	1·210	23·3	1·370	36·9	1·580	53·2
1·091	10·9	1·220	24·2	1·383	37·8	1·597	54·5
1·100	12·0	1·231	25·1	1·397	38·9	1·615	55·9
1·108	12·9	1·241	26·1	1·410	39·9	1·634	57·5

Caustic Soda (Lunge).

Sp. Gr. *at* 15°	% $NaOH$	*Sp. Gr.* *at* 15°	% $NaOH$	*Sp. Gr.* *at* 15°	% $NaOH$	*Sp. Gr.* *at* 15°	% $NaOH$
1·007	0·61	1·060	5·29	1·116	10·06	1·180	15·91
1·014	1·20	1·067	5·87	1·125	10·97	1·190	16·77
1·022	2·00	1·075	6·55	1·134	11·84	1·200	17·67
1·029	2·71	1·083	7·31	1·142	12·64	1·210	18·58
1·036	3·35	1·091	8·00	1·152	13·55	1·220	19·58
1·045	4·00	1·100	8·68	1·162	14·37	1·231	20·59
1·052	4·64	1·108	9·42	1·171	15·13	1·241	21·42

Caustic Soda (Lunge)—Continued.

Sp. Gr. at 15°	% *NaOH*	*Sp. Gr. at* 15°	% *NaOH*	*Sp. Gr. at* 15°	% *NaOH*	*Sp. Gr. at* 15°	% *NaOH*
1·252	22·64	1·320	28·83	1·397	36·25	1·483	44·38
1·263	23·67	1·332	29·93	1·410	37·47	1·498	46·15
1·274	24·81	1·345	31·22	1·424	38·80	1·514	47·60
1·285	25·80	1·357	32·47	1·438	39·99	1·530	49·02
1·297	26·83	1·370	33·69	1·453	41·41		
1·308	27·80	1·383	34·96	1·468	42·83		

3. Alcohol.

Aqueous Solutions (Fownes).

Sp. Gr. at $\frac{15\cdot5^\circ}{15\cdot5^\circ}$	% *by Weight Alcohol*	*Sp. Gr. at* $\frac{15\cdot5^\circ}{15\cdot5^\circ}$	% *by Weight Alcohol*	*Sp. Gr. at* $\frac{15\cdot5^\circ}{15\cdot5^\circ}$	% *by Weight Alcohol*	*Sp. Gr. at* $\frac{15\cdot5^\circ}{15\cdot5^\circ}$	% *by Weight Alcohol*
0·9991	0·5	0·9638	26	0·9135	52	0·8533	78
0·9981	1	0·9623	27	0·9113	53	0·8508	79
0·9965	2	0·9609	28	0·9090	54	0·8483	80
0·9947	3	0·9593	29	0·9069	55	0·8459	81
0·9930	4	0·9578	30	0·9047	56	0·8434	82
0·9914	5	0·9560	31	0·9025	57	0·8408	83
0·9898	6	0·9544	32	0·9001	58	0·8382	84
0·9884	7	0·9528	33	0·8979	59	0·8357	85
0·9869	8	0·9511	34	0·8956	60	0·8331	86
0·9855	9	0·9490	35	0·8932	61	0·8305	87
0·9841	10	0·9470	36	0·8908	62	0·8279	88
0·9828	11	0·9452	37	0·8886	63	0·8254	89
0·9815	12	0·9434	38	0·8863	64	0·8228	90
0·9802	13	0·9416	39	0·8840	65	0·8199	91
0·9789	14	0·9396	40	0·8816	66	0·8172	92
0·9778	15	0·9376	41	0·8793	67	0·8145	93
0·9766	16	0·9356	42	0·8769	68	0·8118	94
0·9753	17	0·9335	43	0·8745	69	0·8089	95
0·9741	18	0·9314	44	0·8721	70	0·8061	96
0·9728	19	0·9292	45	0·8696	71	0·8031	97
0·9716	20	0·9270	46	0·8672	72	0·8001	98
0·9704	21	0·9249	47	0·8649	73	0·7969	99
0·9691	22	0·9228	48	0·8625	74	0·7938	100
0·9678	23	0·9206	49	0·8603	75		
0·9665	24	0·9 84	50	0·8581	76		
0·9652	25	0·9160	51	0·8557	77		

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